Inter-Agency Perchlorate Steering Committee
Analytical Subcommittee Report

Prepared by: Sanwat Chaudhuri, Ph.D.
Utah Department of Health,
Division of Epidemiology and Laboratory Services,
Salt Lake City, Utah

Howard Okamoto
California Department of Health Services
California

Steven Pia
United State Envrionmental Proection Agency
National Environmental Research Laboratory
Las Vegas, Nevada

David T. Tsui, Capt, USAF
Air Force Research Laboratory
Human Effectiveness Division
Toxicology Branch
Wright Patterson AFB, Ohio

On 26 March 1999

ABSTRACT

A successful study was conducted to evaluate the reliability of analytical methods for perchlorate analysis in water. The research study consists of: (1) an evaluation of the existing methodologies for perchlorate analysis; (2) an inter-laboratory collaborative study to evaluate the capability of ion chromatography methods for the analysis of perchlorate ion in water; (3) an evaluation of laboratory and field sampling issues, such as total dissolved solids (TDS), pH, holding time, container type, and interference, which may affect the stability and detection of perchlorate.

Ion chromatography (IC) was identified as the best available technology for perchlorate analysis. An inter-laboratory collaborative study was organized to quantitatively evaluate the performance of existing ion chromatographic methods for the measurement of perchlorate in drinking water and ground water. The Collaborative study (Col-lab) group was composed of 19 laboratories from the commercial, state, and federal sectors, all of who were using IC for perchlorate analysis. The study group represented most if not all the laboratories measuring perchlorate for ongoing monitoring and research. Col-lab samples consisted of well water at three dissolved solids levels, 284-288 parts per million (ppm) (T3), 142-144 ppm (T2), and 71-72 ppm (T1), which were spiked with known concentrations of perchlorates, and two control samples. Spiking concentrations were: 6 parts per billion perchlorate (ppb) (C2T1, 2, and 3), 18 ppb (C3T1, 2, and 3), 36 ppb (C4T1, 2, and 3), and control samples were: a reagent water blank (C1T1, 2, and 3), and a reagent water sample spiked with 51 ppb of perchlorate ion (ST0). The sample labels C1, 2, 3, and 4 indicate increasing perchlorate concentration and T1, 2, and 3 indicate increasing concentration of dissolved solids. Concentration of perchlorate ion in samples was unknown to the participants at the time of analysis.

Two method variants (AS-11 and AS-5) were compared. The distinction was based upon the type of ion exchange column used and the eluent (dilute base with the AS-11 and dilute base + *p*-cyanophenol with the AS-5) with 13 participants using AS-11, 5 using AS-5, and 1 using an FastSep ion exchange column. The reliability of the

method was evaluated based upon the following performance criteria: within laboratory precision (repeatability), between laboratory error, combined within and between laboratory error (reproducibility), and accuracy. Both AS-5 and AS-11 was found satisfactory for perchlorate analysis in typical ground and surface water samples.

In the presence of anions commonly found in ground water and drinking water, the perchlorate stability study showed that perchlorate is stable for at least ten weeks. No degradation of perchlorate was observed when either plastic or glass containers were used, indicating that either type of container may be used for storing samples. The stability study also showed that pH in the range of pH 4 to 10 does not affect the stability of perchlorate; furthermore, pH does not interfere with perchlorate analysis. Hence, additional sample preservation procedures are not recommended in conjunction with perchlorate analysis by ion chromatography.

Anion interference studies on the AS-5 and AS-11 were conducted. The results of the AS-5 anion interference study were presented at the Inter-agency Perchlorate Steering Committee (IPSC) Stakeholders' Meeting, at Henderson, NV. Anion interference on the AS-11 method was studied and the results are presented in this report. Both studies demonstrated that more than twenty-two anions commonly present in aqueous matrices do not interfere with either the AS-11 or the AS-5 method. Additionally, the percent recovery of 20-ppb perchlorate spiked recovery was found to be unaffected by the presence of 1000 ppm carbonate, chloride, and sulfate.

TDS studies showed that perchlorate retention time and detector response was unaffected by low levels of TDS, less than 1000 ppm. However, when TDS concentrations is above 1000 ppm, the recovery of low levels of perchlorate, at or near the detection limit, was poor. Less than 20% perchlorate was recovered from samples containing 5 ppb of perchlorate when either chloride or nitrate was present at concentrations greater than 1000 ppm. No perchlorate was recovered in 5-ppb perchlorate samples containing iodide at a concentration greater than 1299 ppm. Signals corresponding to 5-ppb spiked perchlorate gradually decrease in the presence of 1320- ppm bromide or 1321-ppm phosphate. Low levels of perchlorate could not be detected in samples containing 1300-ppm sulfate spiked with 5-ppb perchlorate.

Additionally, the TDS study also demonstrated that the percent recoveries of perchlorate at elevated concentration, 50 ppb, did not indicate any problem until at the presence of about 6830-ppm TDS. At above 17075 ppm TDS, no perchlorate recoveries were observed in 50-ppb perchlorate spiked samples. High levels of TDS limit the application of ion chromatography for the detection of low levels of perchlorates, at or near method detection limit of 4 ppb, in water. Both the electrical conductivity and total dissolved solids values for a given sample should be used as a prescreening measure. Furthermore, in limited cases where TDS may pose a problem for IC analysis, preparative techniques for the removal of total dissolve solids should be further investigated.

TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

LIST OF ABBREVIATIONS

% V_I	coefficient of variation for between laboratory error
% V_R	coefficient of variation for reproducibility, combined within and between laboratory error
% V_r	the coefficient of variation for repeatability, the within laboratory precision
µg	Microgram
µL	Microliter
µS	micro-siemen
Acc. %	accuracy percent, the ratio of the bias and known value expressed as a percent
ACS	American Chemical Society
AFRL/HEST	Air Force Research Laboratory, Operational Toxicology Branch
AMMS®	Anion Membrane Suppressor System®
ASRS® - Ultra	Anion Self-Regenerating Suppressor® - Ultra
ASTM	American Society for Testing and Materials
Avg.	Average
AWWAF	American Water Works Association Research Foundation
Bias	difference between the measured and known concentration
Bias %	bias percent, the ratio of the bias and known concentration, expressed as a percent
°C	degrees Centigrade
C1, 2, 3 or 4	Concentration labels for study samples, c1 = blank, c2 = 6 ppb, c3 = 18 ppb, c4 = 36, st0 = 51 ppb perchlorate
CAS NO.	Chemical Abstract Services registry number
CDHS	California Department of Health Services

CE	capillary electronphoresis
ClO_4^-	Perchlorate
cm	Centimeter
Col-lab	collaborative study
Conc.	Concentration
CV or % CV	coefficient of variation or percent coefficient of variation
DQOs	data quality objectives
FAA	flame atomic absorption spectroscopy
G_{avg},	grand average of the means of the replicate data
HPLC	high performance liquid chromatography
IC	ion chromatography
IPSC	Inter-agency Perchlorate Steering Committee
K	cell constant
KCl	potassium chloride
KI	potassium iodide
KNO_3	potassium nitrate
KPO_4	potassium phosphate
L	Liter
M	Molarity
MΩ	Megaohm
MDL	method detection limit
mg	milligram
min	Minute
mL	Milliliter
mm	Millimeter
mM	Millimolar
mol	Mole
N	sample size
NaBr	sodium bromide

NaOH	sodium hydroxide
$NaSO_4$	sodium sulfate
ng	Nanogram
NO_3^-	nitrate anion
NTS	Nevada Test Site
pCi	pico curie
pg	Picogram
ppb	parts per billion or micrograms per liter (µg/L)
ppm	parts per million or milligrams per liter (mg/L)
PQL	practical quantitation limit
QC	quality control
RFP	request for proposals
RL	reporting limit
S_l	between laboratory error
S_r	repeatability, the within laboratory standard deviation or precision
S_R	reproducibility, the combined within and between laboratory error
S_x	standard deviation of the grand average
Std. Dev.	standard deviation
T1,2, or 3	concentration of dissolved solids in the sample, t1 = 71-72 mg/L, t2 = 142-144 mg/L, t3 = 284-288 mg/L
TDS	total dissolved solids
UDOH	Utah Department of Health
USEPA	United State Environmental Protection Agency
USEPA/NERL	United States Environmental Protection Agency, National Environmental Research Laboratory
UV	ultra-violet

SECTION I

INTRODUCTION

SECTION I: INTRODUCTION

The Inter-agency Perchlorate Steering Committee (IPSC) analytical sub-committee was formed in January 1998. The analytical subcommittee consists of four co-chairs: Dr. Sanwat Chaudhuri from Utah Department of Health Laboratory at Salt Lake City; Howard Okamoto California Department of Health (CDHS), Steven Pia, United State Enviornmental Protection Agency/ National Environmental Research Laboratory (USEPA/NERL) at Las Vegas, Nevada, and Captain David Tsui from Air Force Research Laboratory/Operational Toxicology Branch (AFRL/HEST) at Wright Patterson Air Force Base, Ohio. The mandates of the IPSC analytical sub-committee were:

- Evaluate existing methodologies for perchlorate analysis.
- Through inter-laboratory methods validation studies, quantitatively evaluate the variability (bias), robustness and specificity (uncertainty) of the state-of-the-art and most widely accessible technologies and methodologies for perchlorate analysis.
- Evaluate and review laboratory and field sampling issues related to perchlorate analysis, such as eluent composition, pH, total dissolved solids(TDS), stability/holding time, and container for sample storage.

The sub-committee reviewed and discussed pros and cons of existing methods, including ultra-violet (UV) spectrophotometry, flame atomic absorption (FAA) spectrometry, high performance liquid chromatography (HPLC), and ion chromatography (IC). The following technologies were reviewed:

Gravimetry: Numerous gravimetric methods have been reported for the determination of perchlorate ions. In gravimetry, perchlorate is precipitated out of solution by ionic reagents that show high affinity for binding to perchlorate. One of the best known examples of such organic dyes is nitron (4,5-dihydro-2, 4-diphenyl-5-(phenyl-imino)-1H-1,2,4-triazolium hydroxide, inner salt). (Welcher, 1947; Shahine, 1975). In addition to nitron, tetraphenylarsonium (Welcher, 1948; Carr, *et al.,* 1972; Glover, 1965; Kodama, 1963), methylene blue (Atack, 1915; Nabar, 1959),

tetrapyridinecuprate (II) ion (Bodenheimer, 1955), and phthalic acid (Lumme, 1975) have been used. This type of method is time consuming, tedious, and relatively unselective for perchlorate analysis because other anions such nitrate and chloride could be precipitated by the organic dyes. In fact, nitron was originally used for the analysis of *nitr*ate i*on*s; hence, the name.

Ultraviolet (UV) Spectrophotometry: Perchlorate ion is inactive to UV (Yamashita, 1985; Zou, 1991). However, perchlorate can be indirectly detected by UV-spectrophotometry through complex formation with ionic chromatophores, such as brilliant green (Burns, 1989), methylene blue (Kawase, 1979), cuproin (Yamamoto, 1969), amiloride hydrochloride (Burns, 1980), and copper(I)/6-methylpicolinealdehyde azine (Gallego, 1985), which have high affinities for binding to perchlorate. Due to the high extinction coefficient of the chromatophores, this technique allows the detection of perchlorate at the UV spectra range. Hence, the specificity of these UV-spectrophotometric methods is as specific as the chromatophores' binding affinity for perchlorate. In most cases, these chromatophores can bind to other anions as well as to perchlorate, thus, giving a false positive results.

Flame Atomic Absorption Spectroscopy (FAA). Most FAA methods require precipitation of perchlorate prior to analysis by FAA. Flame atomic absorption spectrometry is not specific for perchlorate. Perchlorate is indirectly detected by atomic absorption emission of chloride. Organic compounds that precipitate perchlorate may precipitate certain chloride containing compounds, thus, giving a false positive results.

Ion-Pair High Performance Liquid Chromatography (HPLC). Chromatographic separation of perchlorate from other anion is accomplished by ion-pair reagents. (Zou, 1991). The ion-pair reagents in the mobile phase of the HPLC bind to perchlorate. The affinity of the perchlorate/ion-pair reagent complex for the column resin leads to the retention of the complex. An electrochemical or conductivity detector detects perchlorate as the perchlorate/ion pair reagent complex elutes out

of the column. Current method detection limit for ion specific electrode is not desirable.

Ion chromatography. Ion chromatography or ion exchange chromatography has been widely used in analytical chemistry for the separation of ionic species, which is often followed by the detection of the physical or chemical properties. In the case of perchlorate, it is chromatographically separated from other possible interfering anions and a conductivity detector is often used for detection. Ion Chromatography is state-of-the-art technology and is increasingly being used by analytical laboratories for the analysis of anions. This technique is of particular interest because of its capability to analyze complex mixtures of inorganic anions in a sample. There are no known conclusive data indicating the possibility of false positive results in using this technique to analyze for perchlorate in water.

There are two components to perchlorate analysis, separation of perchlorate from all other species in water, and measurement of the separated perchlorate against suitable standards.

a) Separation. Separation of perchlorate and other dissolved species (anions) in water is based on the attraction (affinity) of perchlorate for a special organic exchanger (ion exchange resin) packed into a column for convenient use. The anions are carried through the column by a flow of solution called the mobile phase or eluent. Anions move through the column according to their affinities for the ion exchange resin and the mobile phase. Anions with higher affinity for the mobile phase and less affinity for the ion exchange resin elute out of the column faster than those anions with lower affinity for the mobile phase and higher affinity for the resin. As a result, the anions move through the column and separate into thin bands. Since the relative strength of an anion's attraction to the ion exchange resin is expected to be different for each dissolved specie, they separate and come off (elute from) the ion exchange column at different times. As the anions pass through the detector, they are registered as peaks with a peak area or peak height proportional to concentration and at a retention time characteristic of the anion. Most method variations occur in column

technology. The IC columns are usually made of a cross-linked polymer containing a back bone polymer with positively charged molecules on the surface. Inorganic ions exchange sites with the positive charges followed by separation from the column. Polystyrene divinylbenzene and ethyl divinyl-benzene, as the back bone polymer, and quaternary ammonium ion, as the positively charged ion, are often used as the column material. To accomplish ion separations, the column properties are often modified by altering the cross-link or the backbone polymer. Perchlorate is a large, polarizable, and relatively hydrophobic molecule. The hydrophobicity of perchlorate (ClO4) and other common inorganic ions is in the decreasing order of ClO_4^- >I- >Br^- > Cl^- > F^-. In order to achieve a good separation of perchlorate, a column with hydrophilic nature is essential. The hydrophilicity of columns manufactured by Dionex is in the order of AS-16 > AS-11 > AS-5 > FastSep > AS-9 > AS-14.

Mixed water types, including wastewater, surface water, storm water, ground water, that contains organic chemicals with high dielectric constant and high TDS, could alter the ionic strength of the ion exchange and affect chromatography and detector sensitivity. The possibility of sample pre-treatment, prior to column separate has been mentioned. However, some studies are being performed on sample cleanup techniques using commercially available ion exchange cartridges to remove anions and cations that interfere with perchlorate analysis, from samples.

b) Detection. The separated bands of anions are detected by the electrical properties created by the combination of the mobile phase and anion in the detector at a given time. The property of a solution to conduct electrical charge is called the conductivity. A conductivity detector measures this property of solution in the detector cell. As the mobile phase with bands of separated anions flows through the detector cell, the difference in the conductivity of the mobile phase and the separated anions is registered and recorded by a computer data system, resulting in an ion chromatogram. The conductivity of the mobile phase becomes the baseline of the chromatogram, and the relatively

higher or lower conductivity of the separated anions results in either peaks or valley on the chromatogram, respectively.

Ideally, only the anion of interest would be present in the small volume of eluent containing the separated band of perchlorate while the eluent would be non-conducting, presenting the lowest background and highest sensitivity. However, the typical mobile phase is conductive and adds to the overall background. Hence, conductive species in the mobile phase are often "suppressed" by a suppresser device. There are numerous type of suppresser devices, including chemical suppressers, electro-chemical suppressers, etc. The most common suppression device used in ion chromatographic analysis of perchlorate is called the Anion Self-Regenerating Suppressor (Dionex Corporation), a form of electro-chemical suppression, operating in the "AutoSupression External Water Mode."

c) Method Variations. Since the need to determine trace levels of perchlorate in various water supplies has become increasing important, a number of method changes have been tried to increase the sensitivity of the IC method. The basic system components remain the same: an ion exchange column, eluent, some method of suppression, and conductivity detection. The hardware (pumps, tubing, materials of construction, the suppresser, and the detector) may affect the sensitivity, accuracy, and reproducibility of the ion chromatographic method but does not contribute directly to the chemistry of the separation. The chemistry of the eluent or mobile phase and the ion exchange resin seem the most promising variables to investigate at this time. Many laboratories and some commercial IC manufacturers are presently engaged in this research and development.

The application of ion chromatography to perchlorate analysis in drinking water has undergone rapid changes in recent years. In 1993, United States Enviornmental Protection Agency (USEPA) published Method 300.0 Determination of Inorganic Anions by Ion Chromatography for the study of inorganic ions using ion chromatograph (Pfaff,

1993). In 1995, Aerojet adapted the technology for perchlorate analysis. With the AS-9 ion exchange column (developed by Dionex Corporation), the method was capable to detect perchlorate at 100 parts per billion. In addition to the AS-9 ion exchange column, other separation columns were also capable of detecting perchlorate (e.g., ALLTECH). However, this detection limit was found inadequate to meet the perchlorate action level of 18 µg/L in drinking water, which was adopted by California Department of Health Services (CDHS).

In early 1997, the California Department of Health Services, Sanitation, and Radiation Laboratory in Berkely (SRL-North) modified an earlier Dionex IC method to achieve a lower reporting limit of 4 ppb (Okamoto, 1997). SRL-North enhanced the earlier Dionex application by increasing the injection volume from 35 µL to 740 µL and optimizing the eluent composition with the addition of 2-mM *p*-cyanophenol in 120-mM NaOH. (Fitchett, 1997; Dionex Application Note) The addition of *p*-cyanophenol has the net effect of decreasing the high adsorption of perchlorate onto the column resin and shortens the retention time. Similar to the earlier Dionex application, the CDHS method utilizes an AS-5 ion exchange column for anion separation, an Anion Membrane Suppressor System® (AMMS) for ion suppression, and a conductivity detector for detecting the separated perchlorate peak. This method became to be known as the CDHS or the AS-5 method. Prior to August 1997, the CDHS method was the recommended method for perchlorate analysis in the State of California.

Acceptable intra-laboratory performance data for the CDHS method were presented at the IPSC-Perchlorate Stakeholders Forum at Henderson, NV, 19-21 May 1998 (Okamoto, 1998). The AS-5 intra-laboratory performance data met the same stringent quality assurance and quality control criteria as the EPA Method 300.0.

However, as reported by various laboratories, the organic modifier, *p*-cyanophenol, which is added to the 120 mM NaOH to decrease the high adsorption of perchlorate in the AS-5 column and shorten the retention time, also caused instrument problems when it is used with an anion suppressor that electrolytically generates regenerant, i.e. Anion Self Regenerating Suppressor (ASRS). Some of the commonly observed instrument problems include excessive base noise, damaged suppressors,

and detector performance degradation (Wang, *et al,* 1998; Sauder, 1998; Shen, 1998). These problems are attributable to *p*-cyanophenol and the suppressor system. *P*-Cyanophenol is electrochemically active. When *p* –cyanophenol is present in an anion suppressor that electrolytically generates the regenerant, such as the ASRS suppressor (which is gradually replacing the older AMMS type suppressor), the oxidized species cause leaching of organics from the suppressor and result in noisy baseline, damaged suppressors, and deterioration of detector response. Hence, the use of *p*-cyanophenol is only recommended when using a suppressor which is chemically regenerated (i.e. AMMS), as described in the original CDHS method (Jackson, 1998). Many laboratories have mistakenly attributed poor observed analytical results to the method rather than the incompatibility of the eluent and instrument.

In response, Dionex Corp. developed the so-called AS-11 method in August 1997, utilizing an AS-11 column which is more hydrophilic than the AS-5. The method employs an AS-11 ion exchange column and dilute sodium hydroxide as the eluent. According to the intra-laboratory data published in American Laboratory, April 1998, the AS-11 method has a reported method detection limit of less then 1 ppb and a laboratory-reporting limit of 4 ppb. Unlike the AS-5 method, the AS-11 method did not require *p*-cyanophenol, and the AS-11 method uses a 1-mL injection loop volume rather than a 740-uL injection loop volume. Since the introduction of the AS-11 method, it has found wider acceptance around the country. In fact, the AS-11 technique was the dominant method employed (13 of 19 participants) by the study participants. This represents a rapid evolution of the method between August 1997 and September 1998 when the collaborative study was completed.

A collaborative study on the method performance of AS-5 and AS-11 are presented in Section II. In the study, samples at different TDS levels were spiked with low levels of perchlorate and sent to 19 laboratories for analysis. Concentrations of TDS and perchlorate in samples were unknown to the laboratories. The data and results are summarized in this report.

The stability of perchlorate in the collaborative study samples, with respect to pH and container types, is presented in Section III.

The potential interference by other ions on the analysis of perchlorates was investigated. Two separate studies were performed, one with an AS-11 and the other with an AS-11 separation column and an IC instrument manufactured by Dionex. The study with AS-5 column was performed by CDHS and presented at the Henderson IPSC meeting on May 18, 1998 (Okamoto, 1998). The study with AS-11 was performed by Dionex Corporation and is presented in Section IV. Both studies tested the interference on perchlorate analysis by twenty-two ions.

The effects of method and sampling parameters, such as pH, methanol, TDS, and conductivity on the performance of AS-11 method were studied. Results are shown in Section V.

The content of this work addresses issues specified in the American Water Works Association Research Foundation (AWWAF) request for proposal (RFP) 2533, Survey the Performance of the CDHS (Ion Chromatography) Analytical Protocol, in providing 1) Gathering available laboratory performance data (inter-lab and intra-lab QA/QC data) 2) Address lessons learned relative to analysis for perchlorate. 3) Evaluate information pertinent to performance of the method, identifying apparent difficulties due to factors such as water quality, possible interferences, or high or low perchlorate concentration effects.

SECTION II

COLLABORATIVE STUDY

Directed by

Stephen Pia

United States Environmental Protection Agency

National Environmental Research Laboratory

Las Vegas, Nevada

In conjunction with

David Tsui, Sanwat Chaudhuri and Howard Okamoto

Under the auspices of the Inter Agency Perchlorate Steering Committee

SECTION II: COLLABORATIVE STUDY

INTRODUCTION

This report contains the results of a collaborative study conducted by IPSC Analytical Sub-Committee, through EPA's, Office of Research and Development, National Exposure Research Laboratory, Environmental Sciences Division Las Vegas, Environmental Chemistry Branch. The purpose of the collaborative (Col-lab) study was to quantitatively evaluate the performance of two existing ion chromatographic methods based upon a round-robin study for the measurement of perchlorate in drinking water.

The first method, the CDHS method, was developed by the California Department of Health Services, Sanitation and Radiation Laboratory in Berkeley. (Okamoto, 1997) Prior to August 1997, the CDHS method was the recommended method for perchlorate analysis in the State of California. The CDHS method was based on an earlier Dionex IC method that had a higher method detection limit of 100 ppb. To achieve a lower reporting limit of 4 ppb, SRL-North enhanced the earlier Dionex application by increasing the injection volume from 35 µL to 740 µL and optimizing the eluent composition with the addition of *p*-cyanophenol. Similar to the earlier Dionex application, the CDHS method utilizes an AS-11 ion exchange column for anion separation, an Anion Membrane Suppressor System® (AMMS) for ion suppression, and a conductivity detector for detecting the separated perchlorate peak. Hence, in various literatures, the CDHS is also referred to as the "AS-5" method. The CDHS method employs a 120 mM NaOH + 2 mM *p*-cyanophenol eluant. CDHS presented acceptable intra-laboratory performance data on the CDHS method at the IPSC-Perchlorate Stakeholders Forum at Henderson, NV, 19-21 May 1998.

In August 1997, Dionex Corp. developed the AS-11 method, and in April 1998, Dionex Corporation published the method in the American Laboratory (Jackson, 1998). The method employs an AS-11 ion exchange column with 100-mM sodium hydroxide in water as eluent; hence, the name "AS-11" method. The method avoided the usage of organic eluent and modifier, and unlike the AS-5 method, the AS-11 method uses a 1-

mL injection loop volume rather than a 740 µL-injection loop volume. The intra-laboratory data showed that the AS-11 method has a reported method detection limit (MDL) of less then 1 ppb and a laboratory-reporting limit (RL) of 4 ppb (Jackson, 1998). Intra-laboratory data for both the CDHS and the AS-11 methods met the same stringent quality assurance and quality control criteria as the EPA Method 300.0 (Pfaff, 1993). Since the introduction of the AS-11 method, it has found wider acceptance among laboratories performing perchlorate analysis.

Several evaluations of the methods and method performance of various laboratories have been sponsored by the EPA, United States Air Force, CDHS, Nevada Division of Environmental Protection, Metropolitan Water District of Southern California, Southern Nevada Water Authority, and other. (AWWARF, 1998) These evaluations expressed concerns over the variability, repeatability, reproducibility and reliability of the ion chromatography methods across laboratories.

To evaluate the methods performance across laboratories, the IPSC Analytical Chemistry Subcommittee formulated the study design for the round robin inter-laboratory study. A list of laboratories interested in participating in the study were contacted and screened. At the time of the study, participating laboratories had the following characteristics: 1). Validated ion chromatography system; 2). Validated method at the time of the study; and 3). Analyst experienced in the development of ion chromatographic analysis of perchlorate. Participants in the study represented most if not all of the laboratories, nationwide, measuring perchlorate routinely.

After the laboratories were identified, USEPA/NERL in Las Vegas, NV collected the sample matrix, spiked it with perchlorate, packaged and shipped the samples to the appropriate laboratories. Air Force Research Laboratory/ Operational Toxicology Branch (AFRL/HEST) at Wright Patterson Air Force Base, Ohio and USEPA in Cincinnati characterized the sample matrix. Utah Department of Health (UDOH) Laboratory demonstrated the stability of Col-lab samples, and five laboratories performed the concentration verifications of the study samples.

The results of the matrix characterization, concentration verification, and stability analysis were submitted to the sub-committee for evaluation. Laboratory performance

data on the Col-lab samples were submitted to USEPA, NERL, in Las Vegas for data analysis. The data obtained by the participating laboratories was evaluated by the subcommittee for precision and accuracy.

In this report, reliability was defined by several method performance criteria: within laboratory standard deviation or precision (repeatability, S_r), between laboratory error (S_l), combined within and between laboratory standard deviation or error (reproducibility, S_R), accuracy, and bias. The first of these, repeatability, is a measure of the random uncertainty of the method. The between laboratory error (S_l) is the systematic error introduced by the laboratories, the method, and the system used. Reproducibility (S_R) is the combined random uncertainty and the systematic error introduced by the laboratories as they make measurements with one or the other technique and represents the expected range of measurements performed by different laboratories on the same sample. Accuracy is a measure of the agreement to the known value that the study group as a whole was capable of performing. The known values assigned to the study samples were validated independently and were the only parameters requiring assessment independent of study. Bias is the difference between the study groups average for a given sample and the known value for that sample. With the exception of the known values, the remaining performance criteria could not be assessed in the absence of the collaborative study.

The Experimental Section is an overview of how the samples were prepared and the statistics used in the report that may not be familiar to a reader not conversant with collaborative studies and what is entailed. By nature, collaborative studies involve statistics in a variety of ways. The tables in the Results and Discussion Section provide a complete picture of the study results. The text is a non-technical discussion of the various parameters, the working definition, how they are used, and what they mean in the context of the degree of confidence one can have in assigning a concentration to perchlorate in a given sample. In this context, this report is the comprehensive study about the measurement of perchlorate in water by ion chromatography.

It is common practice to maintain confidentially of the participant data in collaborative studies. This encourages wide participation in such studies. Whether

good or bad, should the participants feel their performance would be divulged to the other participants or potential clients, the number of participants would be effected, fewer would participate, and the data would not represent the complete or total data quality to be expected. It is the method performance, resulting from the usual and routine application of the method, that the collaborative study attempts to characterize.

Confidentially also ensures that those who read the report or use the collaborative data are not biased personally towards one or more participants. The data and results are accepted and evaluated as a whole. Outlier tests based on the study data quality objectives and judgement of the study referee tend to trim the group to a dimension representing the study group. Not knowing which participant did what frees the reader from bias, for or against, toward the study group or participant. To ensure confidentially, the codes use in the study was assigned in a random order. Participants will be informed of their code when the report is sent to them. The laboratory is free to share this information in whatever context they wish or feel necessary. Participants in the study are listed in Appendix A in alphabetical order,

The data from the study are of such quality that the participant can correct any problems resulting in the rejection of data and specialists can improve the measurement technology for perchlorate in the low parts per billion (microgram per liter) ranges. The method performance characterized by the study gives the larger community targets by which to evaluate changes in method performance due to the modification of one or more method variable. The water used in the study was perchlorate free, represented typical ground water and had typical anions in great excess of the perchlorate concentration. The study results represent the expected performance of the method for typical water matrixes and should not be construed to be the expected performance for other matrix types.

EXPERIMENTAL

Material

The sodium perchlorate was purchase from Aldrich in February 1998, lot number: AR 06730TQ, having the following specifications:

Aldrich product number: 41,024-1
Formula: $NaClO_4$
Melting Point 468^0F
Assay 98.0-102.0 %
pH (5%, 25^0C) 6.0-8.0
Insolubles ≤ 0.005%
Cl^- ≤ 0.003%
SO_4^{2-} ≤ 0.002%

Purity: ACS reagent 99% [7601-89-0]
Formula Weight 122.44
D 2.499
Ca ≤ 0.02 %
Heavy metals ≤ 5 ppm
Fe ≤ 5 ppm
K ≤ 0.05%

Reagent

The water used to prepare the study samples was collected in February 1998, from a well (4 CP-1) located on the Nevada Test Site (NTS). This well was selected because it was known to have been isolated from atmospheric and ground processes that contribute to the migration of surface compounds into the aquifer. The background tritium concentration in the raw water (< 2 pCi/L) is significantly lower than ground water which is recharged from surface sources, rain, and snow melt (> 30 pCi/L). Because of the long isolation of the water from processes likely to introduce perchlorate, it was unlikely that perchlorate would be present. The data in Appendix F for the C1 samples (negative control) show that the raw water contained no measurable concentration of perchlorate; this is also shown from the validation results and the close agreement of the study grand averages to the known values for each sample.

Collaborative Study Samples

The study samples were prepared at USEPA/NERL, Las Vegas, Nevada. The study samples prepared at three concentrations (C2, C3, and C4) and TDS levels of 284-288 (T1), 142-144 (T2), and 71-72 (T3) ppm. Samples with different TDS were spiked with perchlorate at 0 µg/L (C1), 5.8 µg/L (C2), 17.9 µg/L (C3), and 36 µg/L (C4). A control sample of distilled water spiked with 51 mg/L (ST0) of perchlorate was included.

The study samples were prepared at three concentrations (C2, C3, C4) and three TDS levels (T1, T2, T3), plus sample C1 which was a blank at the three TDS levels, and a spiked distilled water sample, ST0. The concentration of perchlorate was 6, 18, and 36 parts per billion (ppb) for C2, C3, and C4 respectively and 51 ppb for ST0. Sample C1 was a blank. The TDS concentrations as a percent for T1, T2, and T3, were 25, 50, and 100 percent raw waters, respectively. The balance of the volume for T1 and T2 was distilled raw water.

To prepare each concentration/TDS batch, the required mass of water was first prepared or diluted to the required TDS level in a large vat then the required mass was transferred into three separate 30-L tanks. The C1 (no perchlorate added) samples were first prepared in equal numbers from the three water batches. Then a known mass of perchlorate was added to the water matrix starting with T1. The same tank was used for C2, C3, and C4 to minimize cross contamination. After each batch of samples was prepared, the tanks were rinsed with deionized water, washed with dilute laboratory detergent, and thoroughly rinsed again with deionized water followed by raw water and air dried. This procedure was repeated until the T1, T2, and T3 were prepared. The distilled water spike was the last batch prepared as cross contamination of perchlorate would be eliminated by this procedure.

The perchlorate solution used to make the study samples was prepared in a two step procedure owing to the low concentration of perchlorate in the samples. For 6-ppb sample (C2), 6 micrograms of perchlorate was required per liter (6 µg/L) of water. The batch size per sample was 6 liters, which meant the spiked mass of perchlorate was

only 36 μg total. The working solution was prepared from the stock solution so that 1 gram of working solution would equal 36 μg of perchlorate ion.

Sodium perchlorate was stored in a desiccator after the bottle was opened in April 98. The balance was checked with both class S and class C1 weights prior to preparation of the stock and working solutions. All the masses were determined by difference in pre-weighed containers to eliminate buoyancy corrections.

To prepare the stock solution, approximately 0.44 ± 0.01 gram of salt was measured into a plastic weighing boat and allowed to stand for 2 minutes to ensure a stable mass of salt. No perceivable change in mass was noted during the 2-minute period. The salt was transferred to a pre-weighed Teflon bottle containing a known mass of distilled water (approximately 50 grams) and the volume was brought to approximately 100 grams with distilled water. The final mass of the solution and the resulting concentration of perchlorate were determined by difference. The working solution was prepared by diluting approximately 1 gram of stock solution with 99 grams of distilled water in a pre-weighed Teflon bottle by the same procedure used for the stock solution on the day before the sample batches were prepared.

Procedure for Sample Preparation

The scale used to measure the mass of the plastic tanks and water used for the samples was checked with a 25-Kg mass, then a 100-gram mass was added to the 25-Kg mass. The mass of the 100-gram weight was determined by difference. The scale was accurate within ±10 grams of the total. The balance used to determine the mass of working solution added to the mass of water for a given sample batch (C2T1, etc.) was checked with class S weights prior to use.

The required mass of water for a given TDS level was added to a pre-weighed tank and the resulting mass for the water determined by difference. The volume was stirred for 5 minutes then transferred into three, 30 L vats, one each for C2, C3, and C4. A mass of working solution was transferred from the working solution contained in the original Teflon container into a pre-weighed 25 mL glass vial and the approximate mass was added to the water volume. The actual mass of working solution delivered was

determined by difference with a precision of ± 0.2 mg (± 0.02%). After the C1 samples were collected, the water was spiked with perchlorate and stirred for a minimum of 30 minutes, then dispensed into the required number of sample containers. The volume of water was converted by specific gravity to liters. Following these procedures resulted in known perchlorate concentrations in the C2 and C3 samples. Owing to the small concentration of TDS in the raw water (approximately 0.29 grams per 1000 grams of solution, 0.03%), the specific gravity was not a significant correction though it was tracked during sample preparation. The study samples were stored in cardboard boxes, tops closed and at laboratory temperature until shipped to the participants.

Matrix Characterization

The matrix of these collaborative samples was characterized for pH, TDS, anions, and cations. In addition, the samples were validated for perchlorate concentration and stability with respect to time and container type. pH characterization was performed at AFRL/HEST. TDS was characterized by USEPA/NERL, following their laboratory standard operating procedure for TDS analysis. Three laboratories characterized anions and cations. The anions were analyzed with ion chromatography using USEPA Method 300.0, Revision 2.1 (Pfaff, 1993). Cations were analyzed with an inductively coupled plasma (ICP) instrument using Thermo Jarrell Ash AIRIS/Axial Plasma by USEPA method 200.0.

Stability of perchlorate in the sample matrix, with respect to time and container type, was performed by UDOH laboratory (see Section IV). Samples were analyzed every week for three weeks and then after 10 weeks for perchlorate. This was done for samples in both glass and polyethylene plastic containers. All samples were analyzed in duplicate at a minimum along with the laboratory quality controls which include laboratory fortified blanks (LFB), check standards, laboratory fortified matrix, and a five point standard curve. For the study of stability with respect to pH, water at pH 5 and 9 was spiked with 50 and 100 µg/L of perchlorate. Each of the samples was split into two containers, one stored at room temperature and the other at 4^0 C. These samples were analyzed for perchlorate every week for six weeks.

For validation of the perchlorate concentration, Col-lab study samples were selected at random and sent to five laboratories for concentration verifications. They were asked to analyze the samples in duplicate by their usual procedures, employing their usual QC sample procedure and to reanalyze any sample if the QC data quality objectives (DQOs) were exceeded. The laboratories were production laboratories regularly involved in perchlorate analyses and a spectrum of other water and wastewater specialties as well.

Methods

All analyses for the perchlorate collaborative (Col-lab) study were performed using ion chromatography. A small volume of the Col-lab sample was introduced into the ion chromatograph. Perchlorate was then, separated and measured using a system comprised of a guard column, analytical column, suppressor device and a conductivity detector. Nineteen laboratories participated in the collaborative study, of which five laboratories used an AS-5 separation column, thirteen used an AS-11 column and one used a FastSep column for the analysis. Appendix A lists the different method conditions used by laboratories that participated in the collaborative study.

Instructions to Study Participants

The instructions to the laboratories performing concentration validation, cation, and anion, and stability analyses are shown in Appendix C. Briefly, each set of samples contained 13 samples, 12 samples of C1T1-C4T3, and 1 sample of ST0 in glass and plastic containers. Glass containers were used exclusively for the collaborative study. The laboratories were asked to analyze the samples in duplicate, by the sample order specified. The sample order was selected to minimize the potential of cross contamination and provide the best estimates of the perchlorate concentration in each sample. Validation in this case simply confirms that the batches of samples were made to the expected (known) perchlorate concentrations.

The instructions to the study collaborators are shown in Appendix C. The instructions are similar to the instructions to the validating laboratories with respect to

following the indicated sample sequence, and application of their usual QC samples and DQOs. The sample order was designed to examine as many variables as possible. C2 samples were preceded by samples that could affect both accuracy and precision, for example. The samples for a given perchlorate concentration and TDS concentrations were all identical. The analytical sequence followed by the participating laboratories could be examined to determine if performance changes, indicated by bias or performance exceeding the study DQOs, were due to variable perchlorate concentration, variable TDS concentration, time of analysis in the sequence, or a combination of one or more, had occurred. For each sample up to N (the number of responding participants), single measurements were available to determine the magnitude of the effect and the statistical significance of those differences.

Data Processing Procedures

A statistical evaluation of the test results was carried out by the procedures described in E-177 and E-691 of the American Society for Testing and Materials (ASTM) Standards on Precision and Bias for Various Applications, 1985, Second Edition. The standard deviations and other statistical parameters and equations for their calculations are listed below.

The grand average, $G_{avg\,j}$, for sample j was calculated by equation 1.

$$G_{avg\ j} = \frac{\sum_{i=1}^{P} \overline{X}_{ij}}{P} \qquad \textit{Equation (1)}$$

where: $\sum_{i=1}^{P} \overline{X}_{ij}$ = mean for sample j by participant i.

P = number of participants.

The standard deviation, $S_{avg\,j}$, of the G_{avg} for sample j was calculated by equation 2.

$$S_{avg\ j} = \sqrt{\frac{\sum_{i=1}^{P} (\overline{X}_{ij} \quad G_{avg\ j})^2}{P \quad 1}} \qquad \textit{Equation} \quad (2)$$

The standard deviation of duplicate pairs for the individual laboratory, S_I, for sample j was calculated by equation 3, where: $x_{1\ or\ 2}$ are the first and second results.

$$S_{IJ} = \sqrt{\frac{(x_1 \quad x_2)^2}{2}} \qquad \textit{Equation}(3)$$

The within laboratory standard deviation (repeatability), S_{RI}, for the j sample was calculated from equation 4.

$$S_{r_j} = \sqrt{\frac{\sum_{i=1}^{P} S_{ij}^{\ 2}}{P}} \qquad \textit{Equation}\ (4)$$

The between lab standard deviation, S_{ij} for sample j was calculated by equation 5.

$$S_{Ij} = \sqrt{S_{avg}^2 \quad \frac{S_{rj}^2}{n}} \qquad \textit{Equation}\ (5)$$

where: n = number of replicates.

The combined within and between laboratory standard deviation (reproducibility), S_{Rj}, for sample j was calculated from equation 6.

$$S_{Rj} = \sqrt{S_{rj}^2 + S_{Ij}^2} \qquad \textit{Equation}\ (6)$$

The coefficient of variation for repeatability for sample j, % V_{rj} was calculated from equation 7.

$$\%V_{rj} = \frac{S_{rj}}{G_{avg_j}} x100 \qquad \textit{Equation}\ (7)$$

The coefficient of variation for between laboratory precision, % V_{Ij}, for sample j was calculated from equation 8.

$$\%V_{Ij} = \frac{S_{Ij}}{G_{avg\ j}} x100 \qquad \textit{Equation}\ (8)$$

The coefficient of variation for reproducibility, % V_{Rj}, for sample j was calculated from equation 9.

$$\%V_{R\,j} = \frac{S_{R\,j}}{G_{avg\,j}} x100 \qquad \textit{Equation (9)}$$

The accuracy index, % A_j, for sample j was calculated from equation 10.

$$\%A_j = \frac{G_{avg\,j}}{known_j} x100 \qquad \textit{Equation (10)}$$

Bias as the difference between the known value and the measured mean value was calculated from equation 11.

$$Bias = G_{avg\,j}\ Known_j \qquad \textit{Equation (11)}$$

The percent Bias, % Bias, was calculated from equation 12.

$$\%Bias = \frac{G_{avg\,j}\ Known_j}{Known_j} x100 \qquad \textit{Equation (12)}$$

RESULTS

Matrix Characterization

TDS, pH, and anion and cation concentrations of the study samples are shown in Appendix B. TDS measurements of samples showed that the collaborative study samples T1, T2, and T3 had TDS at 71-72, 142-144, and 284-288 ppm, respectively, which were within 5% of the expected value. The pH levels of samples were between 8.0 and 8.8, compared with distilled water pH at 7.7.

The raw water used to prepare the study samples showed low levels of sodium, potassium, calcium, magnesium, silicon, sulfate, nitrate, and chloride as expected in drinking water. The cation and anion concentrations of the raw water have been aggressively monitored from 1957 to 1990. As shown in Appendix B, the ion concentrations in the raw water remained constant. In raw undiluted water, sodium levels were between 46.4 to 48.9 ppm; magnesium, 7.2 to 8.2 ppm; potassium, 4.5 to 4.8 ppm; calcium, 28 to 31 ppm, silicon, 27.5; sulfate, 40.5 to 45 ppm; nitrate, 15.4 to 17.2 ppm; and chloride, 12.0 to 12.2 ppm. In diluted water samples, the measured amounts of ions decreased proportionally with dilution.

Five laboratories independently verified the perchlorate concentrations. The average value of measured perchlorate at each concentration level is shown in Table 2.1. The average measured perchlorate values are within +/-10% of the expected known values.

Table 2.1. Perchlorate concentration verification for collaborative study samples, June 28, 1998

Sample ID	Average Measured Perchlorate Concentration (ppb)	Standard Deviation, (S_x)	Sample Size, (N)	Expected Perchlorate Concentration (ppb)
C2T1	6.50	0.75	5	5.8
C2T2	6.19	0.81	5	5.8
C2T3	6.74	0.87	5	5.8
C3T1	17.8	1.0	5	17.9
C3T2	18.1	1.7	5	17.9
C3T3	18.4	1.9	5	17.9
C4T1	34.1	1.9	5	35.4
C4T2	37.0	4.6	5	36.1
C4T3	35.9	2.9	5	35.8
S/TO	51.4	3.8	10	50.8

Procedures, experimental conditions, and results of the stability study are detailed in Section III. The stability data showed that perchlorate concentration in both glass and plastic containers remain essentially the same over the 10 weeks of study. The coefficient of variation of the perchlorate concentration within the ten-week period was less than 10 percent. Similarly, the plastic container variation of concentration within the 10-week period of study was insignificant. This indicates that glass or plastic containers do not affect stability of perchlorate.

Collaborative Study

Table 2.2 is a statistical summary of the study results. For this table the means and standard deviations of the triplicate data met the following criteria: (1) the standard deviation of the mean was greater than zero, (2) the mean was in control, $\leq 3\ \sigma$ of the known value based on the expected precision, and (3) triplicate results were submitted. An asterisk notes special cases and the rationale is presented below.

Table 2.2. Statistical summary of the study results

Sample ID	S_x	S_r	S_I	S_R	G_{avg}	Known	Acc. %	Bias	Bias %	N
UNITS	ppb	ppb	ppb	ppb	ppb	ppb	Percent	ppb	Percent	
C2/T1	0.74	0.42	0.70	0.82	5.7	5.8	98.3	-0.10	-1.72	16
C2/T2	0.56	0.47	0.49	0.68	5.8	5.8	100.0	0.00	0.00	18
C2/T3	0.74	0.46	0.69	0.84	6.2	5.8	106.9	0.40	6.90	14
C3/T1	1.43	0.66	1.38	1.53	18.0	17.9	100.6	0.10	0.56	17
C3/T2	1.54	0.68	1.49	1.63	17.8	17.9	99.4	-0.10	-0.56	17
C3/T3	1.59	1.75	1.23	2.14	17.9	17.9	100.0	0.00	0.00	18
		0.61*	1.55*	1.66*						16
C4/T1	2.36	1.56	2.18	2.68	35.0	35.4	98.9	-0.40	-1.13	19
		1.11*	2.27*	2.27*						18
C4/T2	2.88	1.35	2.77	3.08	35.5	36.1	98.3	-0.60	-1.66	17
		0.87*	2.84*	2.97*						16
C4/T3	2.80	1.74	2.61	3.14	35.2	35.8	98.3	-0.60	-1.68	18
		1.02*	2.74*	2.92*						17
S/T0	2.61	1.55	2.46	2.90	51.1	50.8	100.6	0.30	0.59	44
		0.97*	2.55*	2.73*						38

Sample	C2T1	C2T2	C2T3	C3T1	C3T2	C3T3	C4T1	C4T2	C4T3	ST0
Units	%	%	%	%	%	%	%	%	%	%
$\%V_r$	7.4	8.1	7.4	3.7	3.8	9.8	4.5	3.8	4.9	3.0
						3.4*	3.2*	2.4*	2.9*	1.9*
$\%V_I$	12.3	8.4	11.1	7.7	8.4	6.9	6.2	7.8	7.4	4.8
						8.7*	6.5*	8.0*	7.7*	5.0*
$\%V_R$	14.4	11.7	13.5	8.5	9.2	12.0	7.7	8.7	8.9	5.7
						9.3*	6.5*	8.4*	8.3*	5.3*

*. indicates the values of S_r, S_I, and S_R, with rejected data removed.

The standard deviation of the grand averages (S_x) would show an increase within a series (T1-T3) under one of following conditions: 1). If some component(s) of the total dissolved solids (TDS) contributed to the nonrandom error of the pooled results; and 2). If the sample proceeding the same sample analyses interfered, or if the time between same sample analysis were factors. With the exceptions noted below in the discussion about the within laboratory precision (S_r), S_x for the pooled results show no such trending. TDS, at levels typical of drinking water and groundwater, was not an interference, no analyte was present which acted as an interference, and the time of analysis of a given sample exerted no observable influence on the results. S_x reflected the nonrandom error introduced by the laboratories, the method, or the ion chromatography system employed.

The within laboratory standard deviation (S_r, repeatability) is the random component of the measurement and represents the pooled replicate precision for the indicated number (N) of means. The S_r is the mean precision of the population and reflects how precise an individual laboratory and method can measure replicates of the same sample. This statistic is calculated from the standard deviation of the mean for each participant. S_r appears to increase within a series for C2 and C3. The magnitude of the change for C2 is not significant. The F ratios of the extreme pairs are shown in Table 2.3. The F ratio is defined by the equation:

$$F = \frac{S_1^2}{S_2^2} \qquad \textit{Equation 13}$$

where $S_{r1} > S_{r2}$ and the ratio is always greater than 1.

Table 2.3. F ratios of trending data

Sample ID.	F ratio	F critical 0.05%	Degrees of freedom
C2T3/C2T1	1.2	2.42	13/16
C3T3/C3T1	7.03	2.29	17/16

At first glance the C3 data appear problematic, in that there is only a 5 percent chance of observing an F ratio greater than 2.29 for the indicated degrees of freedom. The reason for this anomaly results from two sets of data for C3T3 (1K and 5S, see page 29 of Appendix E) where the standard deviation of the replicates is almost 5 ppb each. The pooled S_r is calculated from individual variances, the square of the standard deviations. The sum of the variances for the two results is approximately 50, which unduly inflated S_r when summed with a series of much smaller variances having a sum of approximately 7. In this case the large F ratio was not due to trends within the laboratories or the samples but to large differences in 2 of the 18 laboratories. With these removed from consideration, the results for the indicated parameters are consistent with the other S_r in the C3 series and the trend was no longer present. The same consideration was given to the results for the other samples as a comparison. The changes in S_r are small, except for the example of C3, and more consistent within a series.

As a general rule, when the sum of the suspect variance(s) equaled or exceeded the sum of the of the remaining variances, the data point(s) were rejected. When one or a few data points account for 50 percent or more of the within laboratory uncertainty, the results were obviously biased and would not provide a clear picture for the majority of results. For most of the samples, one or two data points were rejected, for ST0 there were six rejected data points.

The between laboratory precision, S_l, indicates the degree of variation to expect when the same sample is analyzed by different laboratories. S_l is calculated as a weighted-difference of S_x and S_R. The means from which S_x was calculated manifest the total error introduced by the population of laboratories. Subtracting S_R from S_x estimates the error likely to influence the results. For this study, S_l is about the same order of magnitude as the data quality objectives for the study. S_l does not increase within a series, indicating that whatever constituted the source of the additional error was not related to the sample composition. The increase in S_l from C2 to C4 within a series was expected based on the concentration of perchlorate in the sample. Higher concentration has a larger absolute error. Furthermore, the relative difference of S_l and

S_R indicate that S_R alone is not a sufficient indicator of data quality nor does it identify that systematic error may be introduced by the laboratory or the magnitude of the introduced error.

The reproducibility, S_R, is the combined random uncertainty, S_r, and the between laboratory error, S_l. S_R is an index of the expected agreement between laboratories when analyzing the same sample with the total uncertainty taken into account. Table 2.4 is a summary of the 95 percent confidence ranges (2 times S_R) for C2 (6 ppb), C3 (18 ppb), and C4 (36 ppb).

Table 2.4. Ninety-five percent confidence ranges for study samples

Sample ID.	S_R – ppb	95 percent confidence range – ppb
C2	0.8	4.4 – 7.6 (± 27%)
C3	1.6	14.8 – 21.2 (± 18%)
C4	3.0	30.0 – 42.0 (± 17%)

S_R is the average for the T1, T2 and T3, and the ranges are based on 3 times S_R. The results represent a lower limit of the reproducibility and can be used to determine the confidence of a given perchlorate measurement. Taking C3 as an example, two or more laboratories reporting a value between 15 and 21 ppb perchlorate indicates the true value is probably 18 ppb, other factors not with standing. The magnitude of the ranges suggest that some thought must be given to the quality control samples which would be part of the sample batch. The accuracy and precision of a given set of measurements can not be determined on the single laboratory quality control samples. This conclusion is supported by the data in Table 2.5 which shows the ratio of S_R (reproducibility) to S_r (repeatability) in which S_r is substantially smaller than S_R. Because repeatability can not be used to judge the magnitude of a laboratory's reproducibility (they, S_r and S_R, are measures of different components of the total error), some independent method must be employed to determine the reliability of the reported measurements.

Table 2.5. Ratio of S_r to S_R

Sample	C2T1	C2T2	C2T3	C3T1	C3T2
Ratio S_R/S_r	2.0	1.4	1.8	2.3	2.4
Sample	C3T3	C4T1	C4T2	C4T3	ST0
Ratio S_R/S_r	1.2	1.7	2.3	1.8	1.9

Spiked samples, blind to the laboratory, added to a batch of samples is one consideration, and spiked matrix samples is another. As a guideline, and until better data are available, the ranges in Table 2.4 can be used to evaluate data for the concentrations indicated.

The grand average is the pooled average of the individual participant replicate averages. In Table 2.5 no distinction was made between techniques (AS-11 or AS-5). As will be shown, there is no significant difference between the two. For the study group, there were 14 or more averages to calculate the grand average. There is no significant difference between the grand average and the known value. The grand average is also used to calculate the accuracy percent.

Accuracy percent is the ratio of the grand average to the known value expressed as a percent. From the values for accuracy percent in Table 2.2, the overall accuracy percent was 100 ± 4%.

Bias is the difference in ppb between the grand average and the known value. The bias percent is the ratio of the bias to the known value expressed as a percent. In this case where study group accuracy was very close to the known value, the bias percent was expected to be small. N is the number of participant averages used to calculate the performance parameters.

Results for C1T1, 2 and 3 were not included because the reported results were inconclusive (see Appendix F). The detection limit for the blanks was determined by the laboratory based on the low standard in the calibration curve. No attempt was made to measure the C1 samples below that concentration by the laboratories. The lowest

reported standard was 2.5 ppb (participant 5L) and the reported results were ND for the C1 samples. An estimate of the blank concentration is provided based on the grand average results as standard addition samples and plotting the known values (x axis) verses the grand average values (y axis). The y intercept was the estimate of the blank perchlorate concentration. (See Appendix F). The range for the three sample sets was – 0.1 (T2) to 0.4 (T3) with an average for the three samples of 0.2 ppb that represents the upper limit of the perchlorate concentration in the raw water.

Table 2.6 is the pooled results for AS-11, AS-5, and all the individual replicate measurements. In this table a direct comparison can be made by visual inspection of the data. The grand average (GRAND AVG.), is the average of the means for AS-11 and AS-5. Combined data (grand avg., S_x, etc.) is computed from the combined data and all the replicate results reported by the participants that were not outliers. Combined data represents the grand average of all participant replicate means. S_x is the standard deviation of the grand average, N is the number of means use to compute the grand average and S_x. SDV combined data is the standard deviation of all replicate results for AS-11, AS-5, and the combined data, where n is the number of replicates for AS-11, AS-5, and combined data, for the indicated sample.

Table 2.6. Pooled data for AS-11 AS-5 and all the replicate results

DATA	GRAND AVG.	S_x	N	SDV ALL DATA	n
C2T1					
AS-11	5.75	0.66	12	0.72	36
AS-5	5.96	0.64	4	0.62	12
Combined data	5.81	0.62	17	0.69	51
C2T2					
AS-11	5.75	0.59	13	0.70	39
AS-5	5.96	0.51	4	0.51	12
Combined data	5.82	0.56	18	0.67	54
C2T3					
AS-11	6.04	0.69	11	0.77	33
AS-5	5.90	0.32	3	0.38	9
Combined data	6.06	0.63	15	0.72	45
C3T1					
AS-11	17.9	1.2	11	1.3	33
AS-5	18.2	1.0	5	1.2	15
Combined data	18.0	1.1	17	1.2	51
C3T2					
AS-11	17.8	1.4	12	1.4	36
AS-5	17.6	0.8	4	1.2	12
Combined data	17.8	1.2	17	1.3	51
C3T3					
AS-11	18.2	1.7	12	2.1	36
AS-5	17.6	0.6	5	2.0	15
Combined data	18.1	1.4	18	2.0	54
C4T1					
AS-11	34.6	2.6	13	2.7	39
AS-5	36.0	1.5	5	2.6	15
Combined data	35.0	2.4	19	2.6	57
C4T2					
AS-11	36.0	2.1	11	2.2	33
AS-5	36.7	2.4	5	2.9	15
Combined data	36.2	2.1	17	2.4	51
C4T3					
AS-11	35.6	2.6	12	2.7	36
AS-5	35.5	2.1	5	3.2	15
Combined data	35.6	2.4	18	2.7	54
ST0					
AS-11	51.00	1.70	26	1.92	78
AS-5	51.61	1.66	15	2.40	45
Combined data	51.18	1.64	44	2.07	132

Table 2.7 is a comparison of AS-11 and AS-5 by simple statistical tests. The F

ratio, F, is a test of the precision. The Student t test, t, is a test of the means. In all cases the index values (F and t) are smaller than the critical values (Fc and tc) for the stated degrees of freedom. Regarding the precision, there is no significant difference between AS-11 and AS-5. Both are equally precise. There was no significance between the means; they both produced the same mean. Because of the limited degrees of freedom (i.e., 5 of 19 participants used the AS-5 method), confidence in the F statistical test is limited. There was no reason to expect one technique to be more precise than the other but the implication from Table 2.7 is that if there was a difference, the F test was not sensitive enough to identify it. The t test is more robust in that the degrees of freedom of the combined data sets are used. The t values show there is no significant difference in the means of AS-11 and AS-5 for the samples. The degrees of freedom for F, by convention, are DF, numerator over the denominator.

Table 2.7. Statistical comparison of AS-11 and AS-5 techniques

SAMPLE	F	Fc	F DF	t	tc	t DF
C2T1	1.08	8.80	11/3	0.89	2.14	14
C2T2	1.38	8.70	12/3	1.11	2.13	15
C2T3	4.67	19.40	10/2	0.70	2.18	12
C3T1	1.41	6.00	10/4	0.92	2.14	14
C3T2	2.95	8.80	11/3	0.63	2.14	14
C3T3	4.67	6.00	11/4	0.70	2.13	15
C4T1	3.05	5.90	12/4	1.90	2.12	16
C4T2	1.30	6.00	4/10	0.82	2.14	14
C4T3	1.64	6.00	11/4	0.19	2.12	16
ST0	1.04	2.35	25/14	1.65	2.03	39

Table 2.8 is a summary of the accuracy and bias for AS-11 and AS-5. Over all, the accuracy is similar between AS-11 and AS-5 and both are close to the expected precision of the study. The average coefficient of variance (CV) was larger for AS-11 than for AS-5 but no significance can be ascribed to the difference. The larger N for

AS-11 provides for a greater degree of variability than was possible for the AS-5 group. However, if one of the AS-5 values had been significantly inaccurate the AS-5 results would have been skewed.

Table 2.8. Comparison of accuracy and bias for AS-11 and AS-5

	ACCURACY PERCENT		BIAS PERCENT		CV%	CV%
Sample	AS-11	AS-5	AS-11	AS-5	AS-11	AS-5
C2T1	95.9	99.3	-4.1	-0.7	11.5	10.7
C2T2	95.8	99.3	-4.2	-0.7	10.3	8.6
C2T3	95.2	99.4	-4.8	-0.6	12.1	5.4
C3T1	99.2	101.0	-0.8	1.0	6.7	5.5
C3T2	97.7	101.3	-2.3	1.3	8.0	4.4
C3T3	99.7	98.4	-0.3	-1.6	9.5	3.4
C4T1	96.2	99.3	-3.8	-0.7	7.6	4.1
C4T2	97.3	101.5	-2.7	1.5	6.0	6.6
C4T3	97.5	98.7	-2.5	-1.3	7.4	5.9
ST0	101.4	101.3	1.4	1.3	3.3	3.1
AVERAGE	97.6	99.9	-2.4	-0.1	8.2	5.8
±	8.2	5.8	---	---	—	—

± - Calculated as the average of the coefficient of variation of the grand average and S_x for the indicated sample. Outliers and labs reporting insufficient data were excluded.

With the small differences and distinctions identified, the study demonstrated that a fairly diverse group of participants using the popular methods for perchlorate analyses have a similar repeatability (random uncertainty S_r), a similar reproducibility (total combined error S_R), a similar between laboratory error (systematic error S_l), and similar accuracy for a range of samples between 0 – 50 ppb perchlorate in a typical water matrix. Based on the overall results, the reliability of the method has been characterized and the method has been validated within the study parameters.

DISCUSSION AND CONCLUSIONS

A satisfactory multi-laboratory test of analytical methods for the analysis of perchlorate by ion chromatography was demonstrated by the low number of rejected data (> 70 percent were within the study parameters), the characterization of the accuracy (100 ± 4 %), and the between laboratory error (11 % for a sample at 6 ppb, 8 % for a sample at 18 ppb, 7 % for a sample at 36 ppb, and 5 % for a sample at 50 ppb perchlorate) for the method.

Two method variants (AS-11 vs. AS-5) were investigated, showing there was no difference between them based on accuracy (98% and 100%, respectively) and bias (8 % for AS-11 and 6 % for AS-5). There was no correlation noted in the results due to sample matrix, matrix component, or time of analysis. The study also demonstrated that large batches of samples could be prepared with a known perchlorate concentration following general laboratory techniques.

The method has been validated for the analysis of perchlorate in typical ground water. The study was limited in that wastewater or other matrix types containing extremely high TDS were not investigated. With careful consideration to study design, inclusive of spiked samples using matrix of interest, the method may find use for matrixes beyond the scope of the study. Additional evaluation of the data is presented in Section VI.

SECTION III

STABILITY OF PERCHLORATE SAMPLES

SECTION III: STABILITY OF PERCHLORATE SAMPLES

David T. Tsui, Steven E. Dickson, Sanwat Chaudhuri

INTRODUCTION

A collaborative study was conducted by the IPSC Analytical Sub-Committee to evaluate the method performance of AS-5 and AS-11 methods for perchlorate in ground and drinking water. In support of the collaborative study, Utah Department of Health Services, Division of Epidemiology and Laboratory Services examined the stability of perchlorate in collaborative study samples. In addition to the evaluation of perchlorate stability in the collaborative study samples, the stability of perchlorate with respect to pH and container types was also examined and presented in this Section.

EXPERIMENTAL

Test Materials

Primary source of perchlorate was sodium perchlorate purchased from J. T. Baker Secondary source standards was supplied by an external laboratory that was involved in perchlorate analysis. Sodium hydroxide was purchased from Aldrich Chemical Company

Reagents

The eluent used was 57% 100mM sodium hydroxide. Reagent grade sodium hydroxide was purchased from Aldrich-Sigma Chemical Company.

Instrumentations and Analytical Methods

Dionex DX 500 ion chromatograph configured with a GP40 Gradient Pump, CD20 Conductivity Detector, AS40 Automated sampler and an LC20 Chromatography Enclosure with rear loading injection and rear loading injection valve was used. Separation was obtained using a Dionex IonPac AS-11 analytical column and an IonPac AG11 guard column. Anions were detected with suppressed conductivity detection using ASRS ULTRA suppressor, an Anion Self-Regenerating Supprressor. All water used was deionized, reagent grade with 18-MΩ-cm resistivity or better. Dionex Peaknet software was used to perform the data processing. An Orion Research Model 701 A digital IONANALYZER was used for pH measurements.

Stability Studies

Collaborative study samples were prepared at the USEPA/NERL in Las Vegas. A detailed discussion on sample matrix characterization, sample preparation and initial concentration verifications of the collaborative study samples were presented in Section II of this report. Briefly, the study samples were prepared at three concentrations (C2, C3, C4) and at three TDS levels (T1, T2, T3). Respectively, the concentrations of perchlorate was approximately 5.8, 17.9, and 36 ppb for C2, C3, and C4. The TDS concentrations for T1, T2, and T3, was 71-72, 142-144, and 284-288 ppm, respectively. A negative TDS control sample (ST0) was prepared by spiking distilled raw water with perchlorate at 51 ppb. Collaborative study samples were prepared in both glass and plastic containers and the samples were shipped to Utah Department of Health, Division of Epidemiology and Laboratory Services in Salt Lake City, Utah for perchlorate stability analyses.

To determine stability of collaborative samples, aliquots of the samples were analyzed under the same analytical conditions, as described in this Section, starting from 7 July to 17 September 1998. Concentrations of the stability samples were determined on 7 July (day 9), 13 July (day 15), 20 July (day 22), 27 July (day 29), and 17 September 1998 (day 88). For pH study, reagent water at pH 5 and 9 was spiked

with perchlorate at 50 and 100 micrograms per liter. Each sample was split into two containers; one was stored at room temperature and the other at 4^0C. Both sets of samples were analyzed for perchlorate concentration from 18 June to 28 July 1998, for a period of six weeks. All analyses were performed in duplicate along with laboratory reagent blank, laboratory fortified blank, laboratory fortified matrix and a five standard calibration curve, to ensure quality of data.

RESULTS AND DISCUSSION

Stability of Collaborative Samples

Results of the perchlorate stability study samples for both glass and plastic containers are shown in Tables 1 and 2, respectively. True perchlorate concentrations and TDS levels were taken from Section II of this document. Average perchlorate concentrations and standard deviation were calculated for each perchlorate concentration at given TDS level. For plastic and glass containers, average percent recovery for perchlorate was within an acceptable plus/minus ten percent of the true values. Similarly, the coefficient of variation is less than ten percent for all samples, regardless of container types. Hence, perchlorate was stable during the analysis period of at least ten weeks, at given TDS levels, regardless of the container type. Plastic or glass does not affect the stability of perchlorate. pH data presented in Table 3.3 indicate that storage temperature of either 4^0C or room temperature does not affect the stability of perchlorate in samples between pH 5 and 9.

Table 3.1. Stability of collaborative samples in glass containers

	STO	C4T1	C4T2	C4T3	C3T1	C3T2	C3T3	C2T1	C2T2	C2T3
Nominal Concentrations (µg/L)	50.8	35.4	36.1	35.5	17.9	17.9	17.9	5.8	5.8	5.8
TDS Levels (ppm)	0	71	142	284	71	142	284	71	142	284
7/7/98 Day 9	45.7	31.9	31.3	32.0	16.0	15.7	16.0	6.2	5.7	6.0
7/13/98	48.5	35.5	34.3	34.5	17.2	17.1	17.3	6.2	6.2	6.2
7/20/98	43.9	33.2	32.1	32.1	16.1	16.3	16.7	6.5	6.3	6.9
7/27/98	47.8	33.6	32.9	34.4	16.8	16.6	16.6	5.9	6.0	5.9
9/17/98	44.5	31.8	33.2	35.1	17.1	16.9	16.0	5.8	6.0	6.3
Average	46.1	33.2	32.8	33.6	16.6	16.5	16.5	6.1	6.0	6.3
Standard Deviation	2.0	1.5	1.1	1.5	0.6	0.5	0.5	0.3	0.2	0.4
Average % RPD	9%	7%	10%	6%	8%	8%	8%	5%	3%	8%
%CV	4%	5%	3%	4%	3%	3%	3%	5%	4%	6%

RPD = Relative Percent Difference

Table 3.2. Stability of collaborative samples in plastic containers

Samples Identifiers	STO	C4T1	C4T2	C4T3	C3T1	C3T2	C3T3	C2T1	C2T2	C2T3
Nominal Concentrations (µg/L)	50.8	35.4	36.1	35.5	17.9	17.9	17.9	5.8	5.8	5.8
TDS Levels (ppm)	0	71.0	142	284	71.0	142	284	71.0	142	284
7/7/98	46.3	32.7	32.7	33.8	16.6	16.0	17.2	6.2	6.0	6.3
7/13/98	46.3	32.8	33.8	33.2	16.4	16.5	16.7	5.8	5.7	6.2
7/20/98	44.1	30.8	31.9	31.1	15.3	15.5	15.3	5.4	5.4	6.0
7/27/98	46.5	32.5	33.8	33.2	16.2	16.2	16.4	5.5	5.5	6.2
9/17/98	45.0	34.5	35.6	35.9	15.2	16.0	15.6	5.7	5.8	5.9
Average	45.6	32.7	33.6	33.4	15.9	16.0	16.2	5.7	5.7	6.1
Standard Deviation	1.0	1.3	1.4	1.7	0.6	0.4	0.8	0.3	0.2	0.2
Average % Recovery	10%	8%	7%	6%	13%	12%	10%	2%	2%	5%
%CV	2%	4%	4%	5%	4%	2%	5%	5%	4%	3%

RPD = Relative Percent Difference

Stability of Perchlorate With Respect to pH

Results of the pH study are shown in Table 3.3. pH 5 and 9 at either room temperature or 4^0C does not affect the stability of perchlorate. However further studies should be performed to determine the effect of reducing agents such as selected chemicals and biological constituents at these pH levels on the analysis of perchlorate.

Table 3.3. Stability of perchlorate with respect to pH

pH	9	9	9	9	5	5	5	5
[ClO_4^-]	100	100	50	50	100	100	50	50
Temperature	4 °C	RT	4 °C	RT	4 °C	RT	4 °C	RT
6/18/98	98.8	98.6	47.6	49.8	97.1	99.5	49.4	46.5
6/25/98	105	104.3	46.8	49.3	104.9	102.5	48.5	48.4
7/1/98	95.7	97.4	46.1	46.8	96.2	96.9	46.8	48.1
7/21/98	94.1	97.4	44.9	45.8	92.4	95.8	47	46.6
7/28/98	99	101	49.6	52.1	96.8	98.9	52	52.9
Average	98.5	99.7	47.0	48.8	97.5	98.7	48.7	48.5
Standard Deviation	4.2	2.9	1.8	2.5	4.6	2.6	2.1	2.6
% CV	4%	3%	4%	5%	5%	3%	4%	5%

- RT = room temperature

SECTION IV

ANION INTERFERENCE STUDIES

SECTION IV: ANION INTERFERENCE STUDIES

P. E. Jackson and T. Streib

INTRODUCTION

For the determination of perchlorate at low ppb levels in drinking water, ion chromatography is the state of the art technology best available to most analytical laboratory across the country. Two IC methods have been developed for the analysis of low ppb perchlorate level. In April 1997, the California Department of Health Services developed the so-called "AS-5" or "CDHS" method based on a Dionex IonPac® AS-5 column. (Okamoto,1997) The CDHS method uses a 740 mL loop injection, an eluent of 120 mM sodium hydroxide with 2 mM *p*-cyanophenol and suppressed conductivity detection with an Anion MicroMembrane Suppressor (AMMS). In late 1997, the Dionex Application Laboratory developed an updated IC method for perchlorate analysis. The improved method uses a 1-mL loop injection volume with an IonPac AS-11 column, 100-mM hydroxide eluent, and suppressed conductivity detection using an Anion Self-Regenerating Suppressor (Jackson, 1998). Both methods have reported a method detection limit at below 4 ppb for drinking water.

Recently, in addition to drinking water matrix, both methods have been applied to the detection of perchlorate in non-drinking water and wastewater, as well as solid matrices, where potential interferences may affect the methods' performance. To address this issue, the CDHS and Dionex Corp. conducted anion interference studies on the performance of the CDHS and AS-11 IC methods, respectively. The results of the anion interference study on the CDHS method were presented at the Perchlorate Stakeholders' Meeting in Henderson Nevada, 19-21 May 1998 (Okamoto, 1998). The CDHS anion interference study demonstrated that twenty-two anions commonly found in environmental matrices did not co-elute with perchlorate when using the CDHS method. Those anions include arsenate, arsenite, bromate, bromide, carbonate, chlorate, chloride, chromate, cyanide, humic acid, iodate, iodide, molybdate, nitrate, nitrite, *o*-phosphate, *o*-phthalate, selenate, sulfate, sulfite, thiocyanate and thiosulfate.

In addition, chloride, sulfate and carbonate at concentrations between 50 to 1000 ppm do not affect perchlorate recoveries.

The purpose of this study is to investigate potential interference when analyzing trace level perchlorate by the AS-11 method using an IonPac AS-11 column. This study replicates the interference study performed by the CDHS on the IonPac AS-5 column.

EXPERIMENTAL

A Dionex DX-500 ion chromatograph was used for this work. The system was configured with a GP40 Gradient Pump, CD20 Conductivity Detector, AS40 Automated Sampler and an LC20 Chromatography Enclosure. Separations were carried out using an IonPac AS-11 (250 x 4.0 mm) analytical column and an IonPac AG11 (50 x 4.0 mm) guard column. The experimental conditions were as follows: sample loop, 1000 µL; flow-rate, 1.0 mL/min; eluent, 100 mM NaOH. Anions were detected by suppressed conductivity detection using an ASRS-Ultra (4 mm), operated at 300 mA in the recycle mode. All water used was Type I reagent grade water, 18-MΩ-cm resistivity or better. All reagents used were ACS reagent grade unless specified otherwise. All anion standards were prepared from sodium salts unless specified otherwise. A list of reagents and suppliers is shown in Table 4.1.

Table 4.1. Reagent and suppliers.

Reagent	Purity	Supplier
Sodium Hydroxide	Certified, 50% w/w solution	Fisher Scientific
Arsenate	Reagent grade	J.T. Baker
Arsenite	Reagent grade	Fisher Scientific
Bromate	Reagent grade	EM Scientific
Bromide	Reagent grade	Ultra Scientific
Carbonate	Reagent grade	Fisher Scientific
Chlorate	Reagent grade	Fluka
Chloride	Reagent grade	Ultra Scientific
Chromate	Reagent grade	Aldrich
Cyanide (K^+)	Reagent grade	Sigma
Humic acid	Technical Grade	Alrdich
Iodate	Reagent grade	Sigma
Iodide	Reagent grade	J.T. Baker
Molybdate	Reagent grade	Fisher Scientific
Nitrate	Reagent grade	Ultra Scientific
Nitrite	Reagent grade	Alrdich
Phosphate	Reagent grade	Sigma
Phthalate	Reagent grade	Sigma
Selenate	Technical grade	Alfa Products
Sulfate	Reagent grade	Ultra Scientific
Sulfite	Reagent grade	Alrdich
Thiocyanate	Reagent grade	Sigma
Thiosulfate	Reagent grade	J.T. Baker

RESULTS AND CONCLUSIONS

Two different interference studies were performed, similar to those detailed in the study performed by the CDHS using the IonPac AS-5 column. In the first study, the same set of 22 anions tested by the CDHS were injected at the 100 ppb level (in the presence of 20 ppb perchlorate) on the AS-11 column using the conditions described in the experimental section. The results are shown in Table 4.2, while the chromatograms are shown in Appendix F. Under elution conditions stated in the Experimental Section, only cyanide, iodide and thiocyanate showed any significant retention on the AS-11 column. Both cyanide and iodide have retention times at 4.38 minutes. Retention time of thiocyanate is 6.27 minutes. Perchlorate is resolved by three minutes from the nearest eluting anion, thiocyanate, which would not be typically found at high levels in drinking water or ground waters.

Table 4.2. Comparison of the retention times of 22 anions and perchlorate on the Dionex IonPac AS-11 column

Anion	Anion Retention Time (minutes)	Perchlorate Retention Time (minutes)
Arsenate	<4	9.27
Arsenite	<4	9.27
Bromate	<4	9.2
Bromide	<4	9.22
Carbonate	<4	9.18
Chlorate	<4	9.13
Chloride	<4	9.12
Chromate	<4	9.08
Cyanide	4.38	9.08
Humic acid	<4	9.08
Iodate	<4	9.05
Iodide	4.38	9.07
Molybdate	<4	9.07
Nitrate	<4	9.07
Nitrite	<4	9.05
Phosphate	<4	9.07
Phthalate	<4	9.05
Selenate	<4	9.07
Sulfate	<4	9.07
Sulfite	<4	9.08
Thiocyanate	6.27	9.07
Thiosulfate	<4	9.05

In the second study, the effect of ppm levels of common anions on perchlorate recovery was investigated by injecting solutions of 20 ppb perchlorate in the presence of

0, 50, 200, 600 and 1000 ppm chloride, carbonate and sulfate, respectively. A 20 ppb perchlorate spike was used for the recovery studies for the sake of expediency, i.e., less time was required to get the system cleaned out for low detection limit work and the ASRS-Ultra could be operated in the recycle mode when quantifying perchlorate at this level. Appendix G shows the stacked plot of the perchlorate spike in the presence of increasing concentrations of common anions. The recovery of perchlorate in the presence of common anions (relative to the peak area averaged from three injections of a 20-ppb standard) is shown in Table 4.3. These results demonstrate that common anions at concentrations below 1000 ppm have no significant effect on the recovery of low ppb levels of perchlorate.

Table 4.3. Effect of ppm levels of common anions on perchlorate recovery (20 ppb) on the Dionex IonPac AS-11 column

Common Anion	Anion Concentration (ppm)	Perchlorate Recovery (%)
Carbonate	50	96.6
Carbonate	200	98.8
Carbonate	600	92.1
Carbonate	1000	94.2
Chloride	50	92.2
Chloride	200	99.2
Chloride	600	98.7
Chloride	1000	97.4
Sulfate	50	94.4
Sulfate	200	100.0
Sulfate	600	93.4
Sulfate	1000	97.4

SECTION V

METHOD PARAMETERS

SECTION V: METHOD PARAMETERS

Sanwat Chaudhuri, Steven E. Dickson, and David T. Tsui

INTRODUCTION

A series of studies have validated the applicability of current chromatographic methods and laboratory conditions for perchlorate analysis in drinking water. As shown in Section II of this report, an inter-laboratory validation study of the AS-11 and CDHS methods demonstrated that in aqueous matrix with qualities similar to that of ground and drinking water, both methods are sufficient for the determination of perchlorate at 4 ppb. The stability study in Section III showed that perchlorate is stable for more than 90 days. Anion interference studies showed that the chromatographic conditions of both methods are selective for perchlorate over twenty-two other anions (Section IV).

However, recently both the AS-11 and CDHS methods have been applied to the analysis of perchlorate in more complex matrices, such as brines, wastewater and soil, where the qualities and the conditions of the matrices may pose a challenge to current method conditions. The purpose of this study is to evaluate the effects of those conditions that may affect the analysis of perchlorate by ion chromatography.

Those conditions include pH, organic solvents, TDS and conductivity. Sample pH is an important parameter because disinfectants and bleaching agents are often used in the treatment of wastewater, drinking water and industrial wastewater. Depending on the water source and treatment, the levels of pH range widely. The pH range for typical environmental water samples is between 4 to 10. (Atlas 1988) The effect of pH on the detector response and chromatography of perchlorate is investigated in this report.

In addition to the sample pH, the effect of TDS on instrument response is also examined because, in selected regions of U.S., the TDS levels often exceed those examined in the collaborative study. For example, the Department of Environmental Quality Division of Drinking Water and Solid and Hazardous Waste, State of Utah,

conducted a survey of perchlorate and anion concentrations in water wells around Salt Lake City. The survey showed that TDS levels often exceed 1500 ppm. The survey also found that individual anion concentrations for chloride, nitrate, iodide, sulfate and various cations could be found in the hundreds of parts-per-million levels. (Wallner 1998). In the Las Vegas Wash and areas around former perchlorate manufacturing sites, the typical TDS and conductivity levels often exceeds 20,000 ppm and 22,000 μS/cm, respectively. Additionally, in the Colorado River system where perchlorate concentrations ranges from 8 ng/L to 3.7 g/L have been measured, the TDS levels often exceed 2,500 ppm (Urbansky 1998).

The effect of commercial solvents on the detector response and chromatography is unknown. Common solvents, such as methanol, ethanol, methylene chloride, and others have been used extensively in either the preservation of soil waste samples or in the bio-remediation of perchlorate. Some of these solvents have high dielectric constants that may affect the ion strength of the eluent and thereby, possibly affecting the ion chromatography and detector response. Moreover, solvents such as, freons, trichloroethylene and 1,1,1-trichloroethane are often detected in the sites contaminated with perchlorate (Wallner 1998). Thus, it was of interest to determine the affect of those solvents on perchlorate analysis.

EXPERIMENTAL

Reagents:

All reagent water used in this study had 18 MΩ or better resistance. HPLC grade methanol was purchase from Fisher Scientific, Inc. (Fair Lawn, NJ). Sodium hydroxide was purchased from Aldrich Chemical Company (Milwaukee, WI). Traceable conductivity calibration standards used for conductivity and TDS measurements were purchased from Fisher Scientific.

Primary source of perchlorate calibration standards used on instrument 1 was sodium perchlorate purchased from J. T. Baker. An external laboratory that was involved in perchlorate analysis supplied the secondary source standard for instrument 1. Primary perchlorate calibration standards used on instrument 2 were purchased from Sigma Chemical Company (St. Louis, MO). Secondary perchlorate standards were purchased as ammonium perchlorate from Alpha Chemical Company (Ward Hill, MA). Test materials were used without further purification.

Potassium chloride, sodium bromide, sodium bromate, sodium chlorite, sodium chlorate, sodium carbonate, potassium iodide, potassium nitrate, sodium nitrite, sodium sulfate, sodium sulfite, sodium thiosulfate, and potassium phosphate were purchased as reagent grade chemicals from Aldrich-Sigma Chemical Company.

Instrument:

The effects of pH and methanol on perchlorate retention time and response were studied independently on a Dionex DX-500 Ion Chromatograph and a Dionex DX-300 HPLC. The effects of TDS on perchlorate retention time and response were performed on the Dionex DX-300 HPLC only. Methods parameters for both DX-500 and DX-300 are similar to the original AS-11 method parameters as published by *Jackson, et al.* (Jackson 1998)

Method parameters for instrument 1: Dionex DX 500 configured with a GP40 Gradient Pump, CD20 Conductivity Detector, and AS-40 Automated sampler.

Separation was performed with a Dionex IonPac AS-11 analytical column (4.0 x 250 mm), ATC-1 anion trap column, Dionex AG-11 guard column (4.0 x 50 mm), An ASRS Ultra suppressor was used for suppression. Suppressor solution was deionized reagent water. Dionex Peaknet fi software was used to perform the data processing. The eluent used was 57mM sodium hydroxide. An Orion Research model 701-A digital IONANALYZER was used for pH measurements.

Method parameters for instruments 2: Dionex DX-300 High Performance Liquid Chromatograph with a Dionex CDM-3 conductivity detector. An ASRS-Ultra 4mm anion suppresser, operating at 500 mA in the auto suppression-external water mode, was used. The system included a Dionex AI-3500 auto-sampler. Data were collected using Dionex AI-450 software. Dionex IonPac AS-11 analytical column (4.0 x 250 mm), Dionex ATC-1 anion trap column, and Dionex AG-11 guard column (4.0 x 50 mm) were used for separation. The mobile phase, consisting of either 57 mM or 100 mM NaOH in, was set at one mL/min flow rate. The injection loop volume was 1000 µL, and the regenerant flow rate was 10 mL/min. Analysis was performed at room temperature. A Fisher Scientific Accumet fi Model 915-pH meter, calibrated at pH 4.0, 7.0, and 10.0, was used for pH measurements.

A Fisher Scientific Accumet fi Model 150 Titration Controller with a glass conductivity cell (1.0 cm^{-1} cell constant, K) and a thermocouple was used for conductivity measurements. Prior to measurement, the titrator was calibrated with individual traceable conductivity calibration standards at 10.1 micromhos/cm (6.8 ppm), 1003 micromhos/cm (669 ppm), and 10149 micromhos/cm (6766 ppm).

Study Samples

pH Study. Study samples were prepared from reagent water with perchlorate concentration at 50 µg/L. pH of the study samples was adjusted by the addition of either hydrochloric acid or sodium hydroxide. Study samples with pH between 3 to 10 were analyzed for perchlorate with both Method 1 and Method 2. Changes in retention time and detector response were noted. Detector response was measured by observing changes in perchlorate peak area count. Analyses were performed in

triplicate along with laboratory reagent blank, laboratory fortified blank, and laboratory fortified matrix to ensure quality of data.

Methanol Study. In order to determine effect of methanol, known volumes of methanol was added to reagent water spiked with 50-ppb perchlorate. Six samples, each containing 50 ppb perchlorate, were prepared at 0, 5 10, 20 30 or 40 percent of methanol. The samples were analyzed using method 1 and 2. All analyses were performed in triplicate along with laboratory reagent blank, laboratory fortified blank, and laboratory fortified matrix to ensure quality of data.

Dissolved Solids and Conductivity Study. A 17075-ppm stock standard solution was prepared in 1-L volumetric flask containing 25 ppm of sodium thiosulfate and 1550-ppm each of potassium chloride, potassium iodide, potassium nitrate, potassium nitrite, potassium phosphate, sodium bromide, sodium bromate, sodium chlorate, sodium carbonate, and sodium sulfate. The 1-L flask was brought to volume with reagent water spiked with either 5- or 50-ppb ammonium perchlorate. The diluted samples at 68.3, 170.8, 341.5, 683.0, 1707.5, 3415, and 6830 ppm was prepared by diluting the stock standard solution with the appropriate perchlorate spiked water. The stock and diluted dissolved solid samples were checked for conductivity with a conductivity meter and analyzed by method 2 for perchlorate recovery.

Separately, stock standard solutions of potassium chloride, potassium iodide, potassium bromide, potassium nitrate, sodium sulfate, and potassium phosphate at 3400 ppm were prepared in reagent water spiked with 5-ppb ammonium perchlorate. The stock standard solutions were prepared from neat standard chemicals without further purification. The stock standard solutions of each chemical were diluted at 1 to 2, 5, 10, 20, and 50. The samples were checked for conductivity with a conductivity meter and analyzed for perchlorate recovery by method 2 for perchlorate.

RESULTS

Effects of Methanol and pH on Perchlorate Retention Time and Recovery

For this study, instruments parameters and method conditions for both the Dionex 500 and 300 IC systems were kept the same. Both systems used NaOH in water as mobile phase, 1-mL injection loop volume, and ASRS-Ultra suppressor for ion suppression. The method detection limit on both instruments were determined to be 1 ppb or lower, according to guidelines set forth in the Code of Federal Regulations 40, Chapter 1, Part 136, Appendix B.

The effects of pH on perchlorate peak retention time and recovery for both instrument 1 and instrument 2 with 57 mM NaOH eluent are shown in Table 5.1 and 5.2, respectively. The data showed very little change in perchlorate retention time and recovery with respect to pH. The retention time and percent recovery data were performed with 50-ppb perchlorate spike concentration. For each pH level from pH 3 to 10, at 1 pH interval, a set of triplicate samples was analyzed. Mean retention time for each triplicate sample was calculated. The standard deviation of each triplicate set was within +/- 0.05 min. The percent coefficient of variation was less than three percent. Percent perchlorate recovery was calculated by dividing the measured mean perchlorate concentration by the expected true perchlorate concentration of 50 ppb. For both instruments, the percent perchlorate recovery stayed within 90-110 percent, demonstrating that pH has little effect on perchlorate recovery for a reagent water matrix. Study also shows that the retention time varies between the two instruments, even though both systems used the AS-11 and same setup parameters for the analysis.

Similar results were obtained for instrument 2, when 100 mM NaOH was used as eluent. From pH levels between 3 to 10, mean retention time for sets of triplicate 50-ppb perchlorate samples showed insignificant retention shift. Furthermore, the percent recent recoveries for 50-ppb spike perchlorate samples were within 90-110 percent. These observations with 100 mM NaOH and those with 57 mM NaOH indicate that pH has little effect with respect to instrument and ionic strength of the mobile phase.

Table 5.1. Effect of pH on ion chromatograph retention time for Dionex-500 IC with an AS-11 IonPac column (57 mM NaOH mobile phase)

pH	Mean Retention Time (min.)	Mean $[ClO_4^-]$ ppb	True $[ClO4^-]$ ppb	Percent Perchlorate Recovery
3.8	12.2	48.4	50	96.4
4.7	12.2	48.2	50	96.4
6.0	12.2	48.2	50	96.4
7.0	12.3	48.2	50	96.4
8.3	12.3	47.2	50	94.4
8.9	12.3	47.7	50	95.4
9.9	12.3	46.4	50	92.8

Table 5.2. Effect of pH on Ion Chromatograph retention time for Dionex-300 IC with an AS-11 IonPac column (57 mM NaOH mobile phase)

pH	Mean Retention Time (min.)	Mean $[ClO_4^-]$ ppb	True $[ClO4^-]$ ppb	Percent Perchlorate Recovery
3.2	9.8	48.2	50	96.4
4.6	9.8	48.6	50	97.2
6.1	9.8	49.2	50	98.4
7.2	9.8	49.7	50	99.4
8.4	9.7	50.7	50	101.3
9.1	9.7	48.2	50	96.4
10.3	9.6	46.4	50	92.8

Effects of methanol on perchlorate retention time and perchlorate recovery on instrument 1 (DX-500) and instrument 2 (DX-300) systems, with 57-mM NaOH mobile phase, are shown in Table 5.3. and 5.4., respectively. Both instruments utilized the ASRS-Ultra suppressor, 1-mL injection loop volume and the same guard and anion column assembly. The instruments varied in the models of the pump system, detector system, and auto-sampler. On the Dionex DX-500 system, with increasing methanol from zero to 40 percent, perchlorate retention times shifted from 12.10 minutes to 12.40 minutes. This shift is insignificant since it is less than three percent. Detector response

is evaluated by the percent recovery of ClO_4, which is the percent perchlorate concentration obtained for samples spiked with 50 ppb of perchlorate. The recovery of perchlorate is slightly affected by methanol. Table 5.3 shows that for sample with no methanol, 101 percent perchlorate is obtained. Samples containing 5% methanol yield only 86.6 % perchlorate. As the amount of methanol in samples increase, the perchlorate recovery reduces, being only 88.3% for samples containing 40% methanol.

Table 5.3. Effect of methanol on perchlorate retention time and recovery on a Dionex-500 IC with an AS-11 IonPac Column and 57 mM NaOH mobile phase

Percent Methanol	Mean [ClO_4^-] (ppb)	True [$ClO4^-$] (ppb)	Percent Perchlorate Recovery (%)	Perchlorate Retention Time (min.)
0	50.5	50	101	12.10
5	43.3	47.5	91.1	12.15
10	41.9	45	93.1	12.20
20	38.8	40	97	12.30
30	35.8	35	102	12.41
40	26.5	30	88.3	12.40

Table 5.4. Effect of methanol on perchlorate retention time and recovery on a Dionex-300 IC with an AS-11 IonPac column and 57 mM NaOH mobile phase

Percent Methanol	Mean [ClO_4^-] (ppb)	True [$ClO4^-$] (ppb)	Percent Perchlorate Recovery (%)	Perchlorate Retention Time (min.)
0	50.1	50	100	8.24
10	49.6	50	99.1	8.14
20	43.7	50	87.4	8.54
30	41.2	50	82.3	8.54
40	35.6	50	71.1	8.54

In comparison, as shown in Table 5.4, with increasing methanol concentration from 0% to 10%, the percent recovery of 50-ppb perchlorate spiked samples, as

observed on a Dionex-300 IC system, remained essentially unchanged, at close to 100%. At 40% methanol, the percent recovery was 71.1%, lower than that observed on a Dionex 500 IC system.

In the original AS-11 method, as described by Jackson *et al*, (1998), the suggested ionic strength of the mobile phase was 100 mM NaOH, significantly higher than the 57 mM NaOH mobile phase described previously. Hence, the effect of methanol on perchlorate retention time and perchlorate recovery was examined with increased ionic strength at 100 mM NaOH eluent on both IC systems, and the results are shown in Tables 5.5. and 5.6.

Table 5.5. Effect of methanol on perchlorate retention time and recovery on a Dionex-500 IC with an AS-11 IonPac Column and 100 mM NaOH mobile phase

Percent Methanol	Mean $[ClO_4^-]$ (ppb)	True $[ClO4^-]$ (ppb)	Percent Perchlorate Recovery (%)	Perchlorate Retention Time (min.)
0	48	50	96	10.84
5	48	50	96	10.84
10	47	50	94	10.89
20	45.5	50	91	10.96
30	46	50	92	10.97
40	45.6	50	91.2	11.0

Table 5.6. Effect of methanol on perchlorate retention time and recovery on a Dionex-300 IC with an AS-11 IonPac column and 100 mM NaOH mobile phase

Percent Methanol	Mean [ClO_4^-] (ppb)	True [ClO4$^-$] (ppb)	Percent Perchlorate Recovery (%)	Perchlorate Retention Time (min.)
0	50.00	50	100.00	6.04
10	50.17	50	100.15	5.92
20	50.58	50	100.96	6.04
30	50.83	50	101.47	6.74
40	49.90	50	99.80	6.3

As shown in Table 5.5 and 5.6, with 100 mM NaOH mobile phase, the perchlorate recovery was unaffected by methanol. On both systems, the percent perchlorate recoveries of 50-ppb spiked perchlorate samples were better than 90% at methanol concentration as high as 40%. Similar effect was observed with ethanol. This indicates methanol and ethanol does not effect the detection of perchlorate. As expected, with increasing NaOH from 57 to 100 mM NaOH, perchlorate retention time shifted from 8.24 to 6.04 minutes on the DX-300 system. Similarly, on the DX-500 perchlorate retention time shifted from 12.1~12.4 to 10.8~11.1 minutes as NaOH concentrations increased from 57 to 100 mM NaOH.

The effect Trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA), which are commonly found to be present in sites where perchlorate is detected (Wallner, 1998) were also investigated. Preliminary study shows that while TCE was not found to affect the perchlorate analysis significantly, TCA was found to have a greater impact on the perchlorate recovery and analysis. A Dionex 500DX instrument was utilized to perform the study. Eluent was 100mM sodium hydroxide 50 µl each of TCA(density =1.34) and TCE (density = 1.46) were spiked into 2 ml each of 50 ppb perchlorate solution. Concentration of TCA in the solution was 35.6 ppm and concentration of perchlorate in the solution was 48.8 ppb. Concentration of TCE in the solution was 32.7 ppm and concentration of perchlorate in the solution was 48.8 ppb.

A reduction in sensitivity of the perchlorate peak was observed, in the presence of either TCA or TCE at the above concentrations. Perchlorate recovery for a sample containing 48.8 ppb perchlorate , and 35.6 ppm TCA or TCE was around 70 percent. Instrument blanks analyzed following these samples showed presence of perchlorate at concentrations up to 10 ppb. A perchlorate solution at 50 ppb concentration containing 2.5 percent of TCA reduced the perchlorate signal significantly, producing a recovery of only 70 % of perchlorate. Reagent water blank analyzed following the TCA and TCE showed the presence of perchlorate. This may be explained by the fact that both TCE and TCA being very hydrophobic in nature was being retained in the system and being eluted only partially and producing low recovery for perchlorate. Further studies need to be performed to evaluate the effects of volatile organic compounds on perchlorate analysis.

Effects of TDS and Conductivity on Perchlorate Retention Time and Recovery

The effects of ppm levels of dissolved solids on 5- and 50-ppb perchlorate recovery are shown in Table 5.7 and 5.8, respectively. The study was performed on a Dionex-300 Ion Chromatograph system, with 100 mM NaOH mobile phase and an AS-11 column. The reporting limit, at three times the method detection limit, was 1.2 ppb. Detector response is expressed as measured perchlorate concentration. The measured perchlorate concentration is calculated from a calibration curve generated by plotting the concentrations of perchlorate standards against the peak area count obtained. The calibration curve was linear from method detection limit to 100 ppb. Conductivity of the samples as measured by the conductivity meter is listed in the tables.

Table 5.7. Effect of ppm levels of dissolved solids on 5 ppb perchlorate recovery on a Dionex-300 IC with an AS-11 IonPac Column and 100 mM NaOH eluent. (ND = Non-detect)

Dissolved Solids Concentrations (ppm)	Conductivity (µS/cm)	Spiked ClO_4^- Concentration (µg/L)	Measured ClO_4^- Concentration (µg/L)	Percent Recovery (%)
0.0	0	5	5.0	100
68.3	101	5	5.1	102

170.8	250	5	5.0	100
341.5	510	5	4.8	96
683.0	1000	5	4.6	92
1707.5	2500	5	1.2	24
3415.0	5100	5	ND	ND
6830.0	10100	5	ND	ND
17075.0	25000	5	ND	ND

Table 5.8. Effect of ppm levels of dissolved solids on 50 ppb perchlorate recovery on a Dionex-300 IC with an AS-11 IonPac Column and 100 mM NaOH eluent. (ND = Non-detect)

Dissolved Solids Concentrations (ppm)	Conductivity (μS/cm)	Spiked ClO_4^- Concentration (μg/L)	Measured ClO_4^+ Concentration (μg/L)	Percent Recovery (%)
0.0	0	50	50.0	100
68.3	101	50	50.2	100.4
170.8	254	50	49.8	99.6
341.5	507	50	49.7	99.4
683.0	1010	50	50.4	100.8
1707.5	2540	50	48.1	96.2
3415.0	5070	50	47.9	95.8
6830.0	10100	50	42.3	84.6
17075.0	25010	50	ND	ND

With respect to increasing dissolved solids concentrations from 0 to 17075 ppm, no significant perchlorate retention times shift was observed in either 5- or 50-ppb perchlorate samples. However, the detector response, as measured by perchlorate concentration gradually, decreases as the conductivity of the samples is increased. As shown in Table 5.5 For the 5-ppb perchlorate spiked samples, detector response showed dramatic deterioration as the conductivity of the samples reached 683 ppm or 1000 μS/cm. At 1707.5 ppm or 2540 μS/cm only 1.2 ppb of perchlorate, or 24% perchlorate recovery, was observed. In samples with 3415 ppm dissolved solids and conductivity higher than 5100 μS/cm, no signal was observed. For the 50-ppb perchlorate spiked samples, deterioration of the detector response was observed at

10100 μS/cm. No detector response was observed at conductivity above 25,910 μS/cm.

The 5-ppb perchlorate spiked study samples with varying concentrations of individual anions, including potassium chloride, potassium iodide, sodium bromide, potassium nitrate, sodium sulfate, and potassium phosphate, were analyzed and the results are shown in Table 5.9. Conductivity of the selected anion concentrations shown in Table 5.9 were measured per conditions described in the Experimental Section. No significant shift in perchlorate retention time was observed in the presence of the salts. Consistent with the results obtained in the anion interference study (Section VI), the percent recovery of 5 ppb perchlorate is unaffected by the presence of low concentrations of chloride, iodide, bromide, nitrate, sulfate, and phosphate. In solutions with less than 1000 ppm and conductivity of less then 1000 μS/cm, nearly 100% recovery was observed. Percent recoveries of 5-ppb perchlorate spike samples are affected by the presence of high anion concentrations. Less than 20% perchlorate recovery was observed in samples with chloride and nitrate concentrations greater than 1030 ppm. No perchlorate signal was observed in samples with iodide concentration at 1298.8 ppm. Perchlorate signals gradually decrease in the presence of 1320 ppm bromide, 520 ppm sulfate and 1321 ppm phosphate.

Table 5.9. Effect of ppm levels of chloride, iodide, bromide, nitrate, sulfate, and phosphate on 5-ppb perchlorate recovery on a Dionex-300 IC with an AS-11 IonPac Column. (ND = Non-detect).

Salts	Total Salt Concentrations (ppm)	Anion Concentrations (ppm)	Conductivity (μS/cm)	Percent Perchlorate Recovery (%)
KCl	0	0	0	99
KCl	68	41	61	102
KCl	170	103	153	100
KCl	340	206	306	96
KCl	679	412	612	92
KCl	1698	1030	1530	20
KCl	3396	2060	3060	ND
KI	0	0	0	98
KI	68	52	78	90
KI	170	130	195	92
KI	340	260	390	94
KI	680	520	779	92
KI	1699	1299	1948	ND
KI	3398	2598	3896	ND
NaBr	0	0.0	0	98
NaBr	68	52.8	79	90
NaBr	170	132.1	198	92
NaBr	340	264.2	396	94
NaBr	680	528.4	793	92
NaBr	1701	1320.9	1981	89
NaBr	3402	2641.8	3963	ND
KNO_3	0	0.0	0	98
KNO_3	68	49.6	72	90
KNO_3	170	124.1	180	92
KNO_3	340	248.2	360	94
KNO_3	680	496.4	720	92
KNO_3	1701	1241.0	1799	30
KNO_3	3402	2482.0	3599	ND
$NaSO_4$	0	0.0	0	99
$NaSO_4$	68	54.9	71	95
$NaSO_4$	170	137.2	178	94
$NaSO_4$	340	274.4	357	96
$NaSO_4$	680	548.8	713	94
$NaSO_4$	1700	1371.9	1783	47
$NaSO_4$	3400	2743.8	3567	ND

KPO_4	68	54.7	77	99
KPO_4	170	136.9	192	99
KPO_4	340	273.7	383	96
KPO_4	680	547.4	766	92
KPO_4	1700	1368.5	1916	ND
KPO_4	3400	2737.0	3832	ND

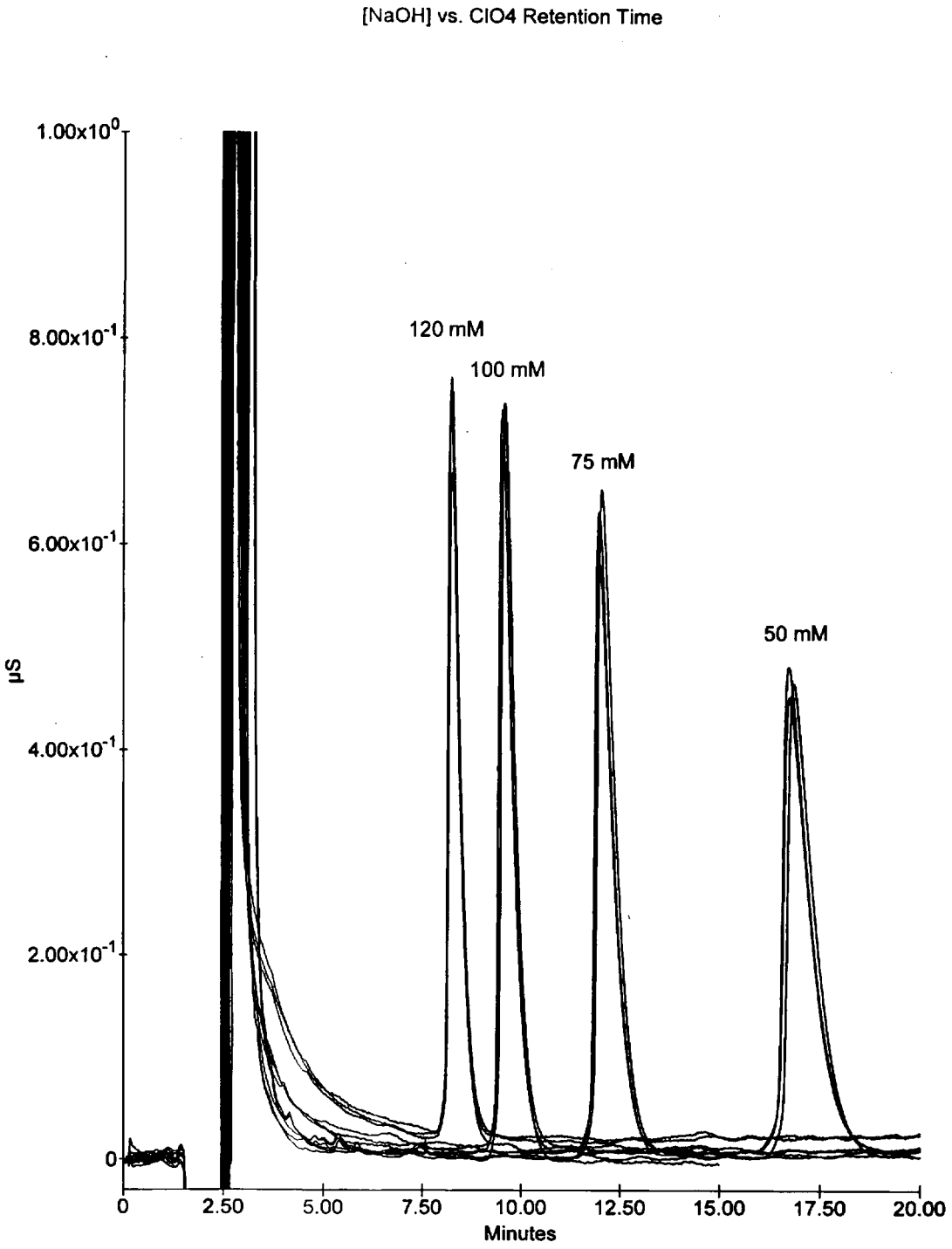
Effects of NaOH Concentration on Perchlorate Recovery and Retention Time

The study was performed on a DX-500 instrument as described in the Experiment Section, except that an ED40 was used for detection. For this study, 50 ppb perchlorate spiked samples was prepared in triplicate and analyzed with mobile phase running at 50, 75, 100, and 120 mM NaOH. The average retention time, area response, and peak height were recorded and presented in Table 5.10, and the chromatograms are shown in Figure 5.1. As shown in Table 5.10, with increasing ionic strength in the mobiles from 50 to 120 mM NaOH, perchlorate retention time shifted from 16.78 to 8.37 minutes. Also, with increasing NaOH concentrations, perchlorate peak-width decreased (Figure 5.1) as peak height increased from 4518 to 8275; however, the area count showed a decreasing trend. This is due to the band broadening of the perchlorate peak in low ionic strength mobile phase.

Table 5.10. Effect of mobile phase strength on perchlorate retention time, response and peak height

[NaOH], mM	Average Retention Time (min)	Standard Deviation	%CV
50	16.78	0.052	0.3
75	12.01	0.029	0.2
100	9.55	0.024	0.2
120	8.37	0.160	1.9
[NaOH], mM	Average Area Count	Standard Deviation	%CV
50	206864.67	6330.726	3.1
75	194239.00	10992.350	5.7
100	180535.67	3154.702	1.7
120	156868.00	1794.660	1.1
[NaOH], mM	Average Peak Height	Standard Deviation	%CV
50	4518	123.5	2.7%
75	6097	314.8	5.2%
100	7242	80.9	1.1%
120	8275	124.8	1.5%

Figure 5.1. Chromatograms of 50 ppb perchlorate spiked samples analyzed in varying concentrations of NaOH mobile phase



SECTION VI

CONCLUSION

SECTION VI: CONCLUSION

A satisfactory survey of the perchlorate method has been performed. The survey included a collaborative study of ion chromatography methods for the detection of perchlorate in drinking water and an evaluation of field and laboratory issues that may affect the methods performance. The method variations were differentiated by the columns. Three different analytical columns were used by the participating laboratories: AS-5, AS-11 and FastSep. The performance of FastSep column could not be evaluated, since there was only one laboratory using this column. The performance of both AS-5 and AS-11 columns were found satisfactory for the analysis of perchlorate in drinking water. However, the methods performance decreases as the concentration of total dissolved solids in sample increases, particularly at low perchlorate levels close to the method reporting level of 4 ppb of perchlorate.

Tables 6.1 through 6.3 represent a summary of performance by the participating laboratories at three perchlorate concentrations and at three different TDS levels. C2, C3 and C4 are the three concentration levels that were spiked into samples having T1, T2 and T3 TDS concentrations. The concentrations of C2, C3 and C4 are shown in the Tables 6.1 through 6.3. Sample C1 did not have perchlorate added. Performance of this sample is presented in Section II. ST0 is the control sample, having a known concentration of perchlorate spiked into reagent water. Data for Tables 6.1 through 6.3 have been taken from the Col-lab study presented in Section II and Appendix E.

Tables 6.1 to 6.3 contain the known perchlorate concentration in samples prepared. Mean ClO_4^- represents the average concentrations (each concentration is an average of the triplicate analyses for each sample) obtained by 19 participants. Standard deviation is calculated from the 19 data points. Percent coefficient of variation represents the variability in method and is obtained by dividing the standard deviation by the mean (Section II). Table 6.1 shows the performance by laboratories at the high concentration and at the three TDS levels. Similarly, Table 6.2 and 6.3 reflects performance at the middle and low concentrations perchlorate with varying TDS concentrations, respectively.

Table 6.1. Laboratory performance at C4 perchlorate concentration

Sample Identification	Known $[ClO_4^-]$ (ppb)	Known TDS (ppm)	Mean $[ClO_4^-]$ (ppb)	Std. Dev.	Variance	Percent Coefficient Of Variation
C4T1	35.4	71	35.0	2.36	5.55	7
C4T2	36.1	142	35.5	2.88	8.28	8
C4T3	35.5	284	35.2	2.80	7.85	8
ST0	50.8	0	51.8	3.77	14.2	7.3

Table 6.2. Laboratory performance at C3 perchlorate concentration

Sample Identification	Known $[ClO_4^-]$ (ppb)	Known TDS (ppm)	Mean $[ClO_4^-]$ (ppb)	Std. Dev.	Variance	Percent Coefficient Of Variation
C3T1	17.9	71	18	1.43	2.05	8
C3T2	17.9	142	17.8	1.54	2.36	9
C3T3	17.9	284	17.9	1.59	2.53	9

Table 6.3. Laboratory performance at C2 perchlorate concentration

Sample Identification	Known $[ClO_4^-]$ (ppb)	Known TDS (ppm)	Mean $[ClO_4^-]$ (ppb)	Std. Dev.	Variance	Percent Coefficient Of Variation
C2T1	5.8	71	5.7	0.74	0.55	13
C2T2	5.8	142	5.7	0.79	0.62	14
*C2T3	5.8	284	6.2	1.75	3.05	29

*2 laboratories reported no or incomplete data for this sample

For the mid and high levels of perchlorate samples, laboratory performance was good as noted by the low coefficient of variation for the C3 and C4 samples. However, at the low concentration there is a significant increase in variability, as evident from the high coefficient of variation for C2 samples. The greatest percent CV is obtained for the C2T3 samples, which had the highest TDS and the lowest perchlorate concentration. It

was noted that for C4T1, all laboratories reported values which were within 10 percent of the known values, whereas for samples C2T3, only 7 of the 19 participants achieved a value within 10 percent of the known. The best accuracy was obtained for samples with highest perchlorate and lowest TDS values; least accuracy was observed with samples C3T3, which had the highest TDS and lowest perchlorate concentration, indicative of the effect of high TDS on perchlorate analysis near the detection limit. A similar effect was observed in the TDS study.

Table 6.4. IC Column performance with T3 samples

Sample Identification	Known [ClO4⁻] (ppb)	Total Number of Laboratories	Number of AS-5 within 20%	Number of AS-11within 20%	Number of FastSep within 20%
C4T3	35.8	19	5 of 5	13 of 13	1of 1
C3T3	17.9	19	5 of 5	13 of 13	1of 1
C2T3	5.8	19	3 of 5	11 of 13	1of 1

Performance of the method with T3 samples using three different columns is presented in Table 6.4. Table 6.4 shows accuracy of the methods using AS-5, AS-11 and FastSep columns at the high TDS level and the varying amount of perchlorate. Data represent the number of laboratories which reported perchlorate concentrations within 20 percent of the known. It is found that all laboratories can achieve 20 percent of the true value at high perchlorate concentrations. At low concentrations, not all laboratories can achieve this accuracy with either method. Two out of the five laboratories that were using AS-5 column reported data that were incomplete and had low perchlorate recovery. Similarly, two of the thirteen laboratories using AS-11 reported low values for perchlorate for samples with high TDS and low perchlorate concentration. It is difficult to evaluate the performance of FastSep column based upon this study alone, since there was only one laboratory using this column.

Although both AS-5 and AS-11 methods provide accurate and reproducible results for drinking waters, most analytical laboratories have switched from the AS-5 method to the AS-11 method due to the ease of use and the ruggedness of the AS-11

method. In fact, at the end of the collaborative study, 13 of the 19 participating laboratories used the AS-11 method. The switch is understandable considering the changes in anion suppression and eluent generation technologies. The newer electrochemically based anion suppression technology (ASRS) which provides better anion suppression than the older chemically based ion suppression (AMMS) is incompatible with the organic modifier, p-cyanophenol, called for by the AS-5 method. Additionally, the new eluent generator designed to generate eluent with more reproducible ionic strength is incompatible with p-cyanophenol and can not generate OH^- above 100 mM. Furthermore, it s been demonstrated that for samples with high TDS, the AS-11 is more rugged, less likely to provide false negatives and false positives (Eaton, 1998).

In addition to the methods performance on drinking water samples, factors concerning laboratory and field sampling issues were examined as well. Section III Stability Study demonstrated that common inorganic ions in water do not interfere with the stability of perchlorate and that perchlorate is stable for at least ten weeks when stored at 4°C. No degradation of perchlorate was observed when either plastic or glass containers were used for storing samples containing perchlorate. This observation is consistent with previous perchlorate stability studies conducted by AFRL in support of the 90-Day Ammonium Perchlorate Toxicity Study (Tsui *et al.*, 1998). In the study, the data demonstrated that aqueous ammonium perchlorate solution at 0.05 and 200 ppb is stable beyond 109 days in the presence or absence or light.

Furthermore, the pH study presented in Section IIII demonstrated that water at pH 5 to 9 had no effect on the stability of perchlorate ion. Reagent water samples at pH 5 and 9, spiked with 50 and 100 ppb of perchlorate, were analyzed every week for five weeks. Insignificant change in concentration of perchlorate with time was observed. Similar results were obtained for samples stored both at 4^0C and at room temperature. This indicates that the pH between the range of 5 and 9, at both 4^0C and room temperature, does not affect stability of perchlorate. The data also show that pH does not affect the retention time or perchlorate response, indicating no effect on the method.

The inorganic anion interference studies with AS-5 and AS-11 columns indicate negligible interference due to commonly found anions up to 1000 ppm on samples with perchlorate concentrations around 20 ppb. Nonetheless, documented cases of interference with similar retention times as that of perchlorate has been reported. To illustrate, chromatograms of a field sample (collected from the Las Vegas Wash area known as French Drain) and the same sample spiked with 20 ppb perchlorate are shown in Figure 6.1 and 6.2 (Eaton 1998; Pohlmann 1998). Both samples were analyzed by the AS-11 method; in this method, the retention time window for perchlorate standard is between 9.1 to 9.8 minutes. The retention time of the unknown peak (labeled as Peak 1 in both figures) is 9.10 minutes and falls within the retention time window of perchlorate standard. Without the matrix spike, as shown in Figure 6.2., the unknown peak was misidentified as that of perchlorate. The chromatogram of the matrix spike samples confirmed the unknown peak as an interference.

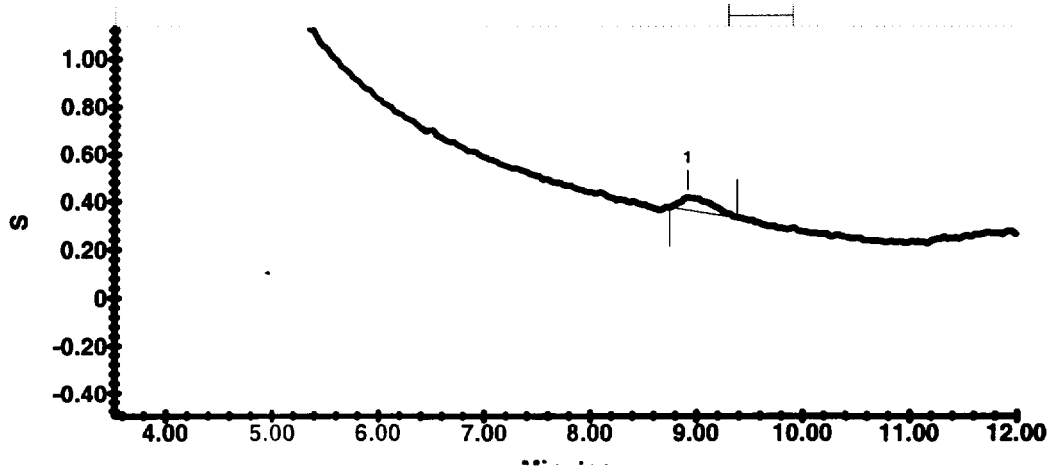


Figure 6.1. An ion chromatogram of a field sample collected in the Las Vegas area (Reprint with permission from Montgomery Watson Laboratories and American Water Works Association Research Foundation.)

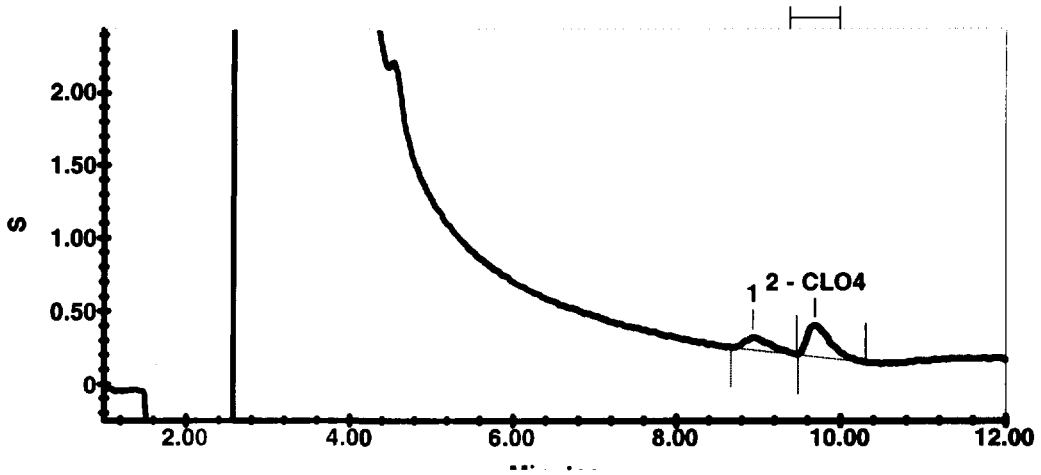


Figure 6.2. An ion chromatogram of the same sample as in Figure 6.1 with 20 ppb ClO_4^- spike (Reprint with permission from Montgomery Watson Laboratories and American Water Works Association Research Foundation)

In addition to the inorganic anion interference study, preliminary studies on potential interference from organic sources were conducted, since hydrophobic solvents such as TCE and TCA which are often present at the same site as perchlorate may interfere with perchlorate analysis. Preliminary study shows that while TCE was not found to affect the perchlorate analysis significantly, TCA was found to have a greater impact on the perchlorate recovery and analysis. Interference due to such organic solvents on perchlorate analysis is currently being further investigated by AFRL/HEST and UDOH/DELS.

The TDS study showed that for the AS-11 column, significant signal deterioration was observed for the detection of perchlorate near the instrument detection limit when samples have high TDS values. Stack plots of chromatograms of 5 and 50 ppb perchlorate spiked in increasing amounts of TDS are shown in Figure 6.3 and 6.4, respectively. The peaks of 5 and 50 ppb perchlorate spike samples can not be accurately integrated when the TDS reaches above 1000 and 10000 ppm, respectively. It is clear from the plots that increasing amounts of TDS askew the baseline of the ion chromatograms. Increased amounts of TDS leads to band broadening, decreased perchlorate peak heights, and non-symmetrical peak shape. Hence, peak height should be not use for method calibration. Furthermore, samples with high an TDS and askew baselines can not be accurately quantified. Studies on the use of an additional sample

preparation step for detecting perchlorate in complex matrices with high amounts of TDS are being addressed by AFRL/HEST and DOH/DELS (Tsui, 1999).

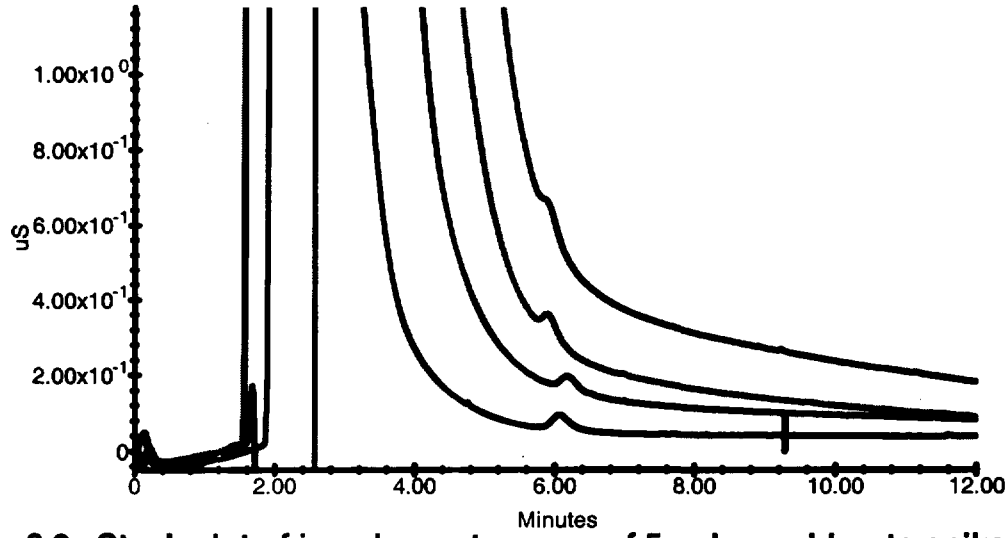


Figure 6.3. Stack plot of ion chromatograms of 5 ppb perchlorate spiked with 250, 500, 1000, and 2000 ppm TDS using AS-11 column

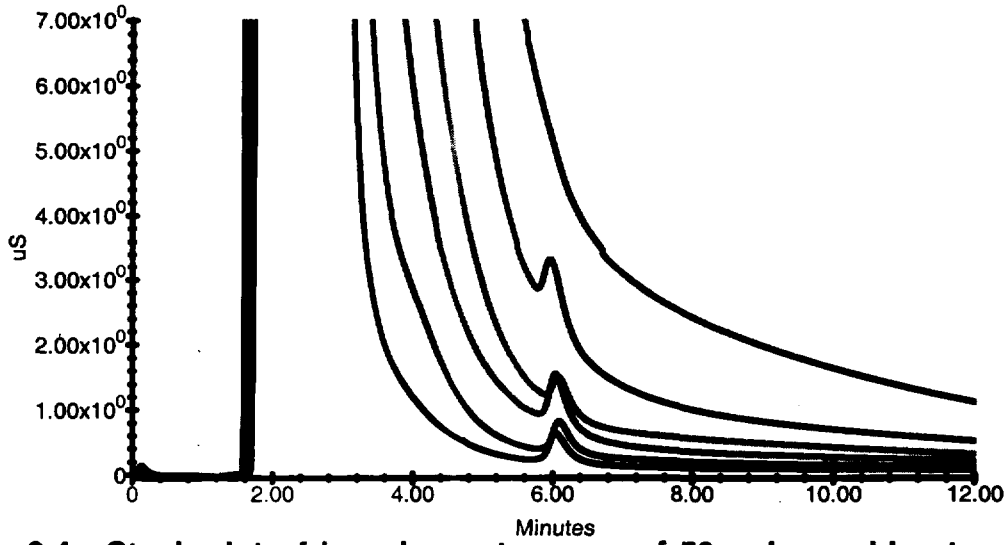


Figure 6.4. Stack plot of ion chromatograms of 50 ppb perchlorate spiked with 500, 1000, 2500, 5000, 10000, and 25000 ppm TDS using AS-11 column

REFERENCES

ASTM. E-177 and E-691 of the American Society for Testing and Materials (ASTM) Standards on Precision and Bias for Various Applications, 1985, Second Edition.

A. Schilt, Perchloric Acids and Perchlorates, The G. Fredrick Smith Company Columbus, Ohio, 1979.

Alltech Chromatography Catalog 300, 1993, All Tech Association Inc. 2051, Waukegan Rd. Deerfield, IL 60015

Atlantis, R. M. Microbiology: Fundamentals and Applications 2 nd ed. Macmillan Publishing Company. 1988.

AWWARF. American Water Works Association Research Foundation. RFP 2533: Survey the Performance of the California DHS (Ion Chromatography) Analytical Protocol. March, 1998.

AWWARF. American Water Works Association Research Foundation. RFP 2534: Short Term Perchlorate Laboratory Issues. March 1998.

Burns, D. T.; Hanprasopwattana, P. *Anal. Chim. Acta.* 1980, *118*, 185-189.

Burns, D. T.; Chimpalee, N.; Harriot, M. *Anal. Chim. Acta.*, 1989, *217*, 177.

Atack, F. W. *J. Soc. Dyers Colour*, 1915, *31*, 183.

Bodenheimer, W.; Weiler, H. *Anal. Chem.*, 1955, *27*, 1293.

California Department of Health Services, Sanitation and Radiation Laboratories Branch. Determination of Perchlorate by Ion Chromatography. Rev. 0, June 3, 1997.

Carr, P. W.; Jordan, *J. Anal. Chem.* 1972, *44*, 1278.

Dionex Corporation. Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography, Application Note 121, Dionex Corporation, 1998.

Dionex Corporation. Record 269, Dionex Chromatography Database 4.2.0, Dionex Corp., Sunnyvale CA, 94086.

E-177 and E-691 of the American Society for Testing and Materials (ASTM) Standards on Precision and Bias for Various Applications, 1985, Second Edition.

Eaton, A.; Haghani A. Analysis of Perchlorate Right or Wrong? Presented at Water

Quality Technology Conference, 1997.

Eaton, A.; Haghani, A.; Cox, N.; Wong, E. A Comparison of the Ruggedness of Different Analytical Methods for Perchlorate. Presented at Water Quality Technology Conference, 1998.

Fitchett, A. Starting Point on the Development of CDHS Method for Perchlorate Analysis [Fax Private communication]. 17 April 1997.

Gallego, M.; Valcarcel, M. *Anal. Chim. Acta.* 1985, *169,* 161-169.

Glover, D. J.; Rosen, J. M. *Anal. Chem.* 1965, *37*, 306.

Jackson, P. Observed Instrument Problems Associated with the Usage of ρ-cyanophenol [Letter Private communication]. April 1998.

Jackson, P. *American Laboratory*, April 1998.

Kawase, J.; Nakae, A.; Yamanaka, M. *Anal. Chem.*, 1979, *51*, 1640.

Kodama, K. Methods of Quantitative Inorganic Analysis. Interscience, New York, N. Y., 1963, pp. 122, 456.

Lumme, P.; Kari, E. *Acta. Chem. Scand. A.* 1975, *29*, 117.

Nabar, G. M.; Ramachandran, C. R. *Anal. Chem.*, 1959, *31*, 263.

Offsite Environmental Monitoring Report: Radiation Monitoring Around United States Nuclear test Areas, Calendar year 1991, pp. 207 and 213.

Okamoto H. S, Perchlorate Stakeholders Forum, Interagency Perchlorate Steering Committee, Henderson, Nevada, May 19-21, 1998

Okamoto, H. Anion Interference Study on A Dionex AS-5 Column. Perchlorate Stakeholders Forum, Henderson, NV. 19-21 May 1998.

Okamoto, H. S. Determination of perchlorate by Ion Chromatography, S.O.P., State of California, Department of Health Services, California, May 1997.

Okamoto, H. S. Anion Interference Study on A Dionex AS-11 Column. Perchlorate Stakeholders Forum, Henderson, NV. 19-21 May 1998.

Pohlmann, B. Ion Chromatograms of Perchlorate Samples Collected from Las Vegas Wash, French Drain [Letter Private communication]. August 1998.

Pfaff, J. D. EPA Method 300.00 Determination of Inorganic Anions by Ion Chromatography, Revision 2.1. United States Environmental Protection Agency, Office of Research and Development, August 1993.

Sauder, C. R. Evaluation of CDHS Method. [Letter] Thiokol Corp. 7 April 1998.

Shahine, S.; Khamis, S. *Microchem. J.*, 1959, *31*, 263.

Shen, Y.; Harrington, P. Observations Concerning the CDHS Method. [Letter] Orange County Water District. 27 April 1998.

Tsui, D.; Narayanan, L; Mattie, D. Stability and Concentration Verification of Ammonium Perchlorate Dosing Solutions. Air Force Tech Report, AFRL-HE-WP-TR-1998-0068. Clearance number ASC98-1914.

Tsui, D.; Clewell, B. Sample Preparation Method for Perchlorate Analysis by Ion Chromatography/the Development of Mass Spectrometric Method for Perchlorate Analysis. Ontario Conference, 18-19 March 1999.

Wallner, W. M.; Cassidy, R.; Chaudhuri, S. [Letter] Survey of Perchlorate and Ionorganic Ions in Water Wells. August 1998.

Wang, H.-C.; Kuo, C. Y. Experiences with the CDHS Method. [Letter to IPSC Analytical Subcommittee] Metropolitan Water District of Southern California. February 1998.

Welcher, F. J. Organic Analytical Reagents, Vol. III. D. Van Nostrand Company, Inc., New York, N.Y., 1947, p. 138.

Welcher, F. J. Organic Analytical Reagents, Vol. III. D. Van Nostrand Company, Inc., New York, N.Y., 1948, p. 326.

Yamamoto, Y.; Okamoto, N.; Tao, E. *Anal. Chim. Acta.* 1969, 47, 127-137.

Yamashita, A.; Azumi, T. *J. Phys. Chem.* 1985, *59*, 5022-5024.

Zou, J.; Motomizu, S.; Fukutomi, H. *Analyst.* 1991, *16*, 1399-1405.

ACKNOWLEDGEMENTS

The following work was a collaborative effort on many levels. The Analytical Chemistry Subcommittee would like to acknowledge the cooperating laboratories without who s timely help the validation and matrix work would not have been possible. Special thanks go to: Ray Wesselman, National Exposure Research Laboratory Cincinnati, Dr. Phil Harrington, Orange County Water District at Los Angeles, Dr. Howard Okamoto, California Department of Health Services/Sanitation and Radiation Laboratory-North, Patricia Watson Southern Nevada Water District, Dr. Kent Richman, American Pacific Corporation Utah, Dr. Sanwat Chaudhuri, Utah Department of Health/ Health Laboratory Services, and Captain David Tsui and Latha Narayanan, United States Air Force/Air Force Research Laboratory.

Special thanks to Patricia Honsa (ORIA), and Robert Hope (ORD SEE) for the preparation of the collaborative study samples on very short notice and who prepared the collaborative study report in less than a week after the closing date of the study, August 3, 19. Without their professionalism and can-do attitude the study would never have been completed in such a short time period. Thanks also to James Mullins who has work with the author to render the mass of data into a usable form.

And special thanks to the 19 participants in the collaborative study, the results of which has moved perchlorate measurement technology to a higher level. The Analytical Subcommittee expresses special thanks to the 19 participants in the study, whose contribution to this project has helped assess the perchlorate analytical method.

Special thanks to Utah Department of Health for their contribution of the stability, pH, methods parameter and Col-lab sample validation study, Air Force Research Laboratory for helping design the study and contribution towards the stability, pH and Col-lab sample validation, California Department of Health for Col-lab sample validation, National Environmental Research Laboratory USEPA, Las Vegas for preparing Col-lab samples, TDS measurements and conducting the study, USEPA, Cincinnati for cation and anion analyses and Dionex Corporation for the interference study.

The authors expresses thanks to Robert Mayhew who helped with the pH study and Robert Lo, who helped in preparing the charts without which the study would have

not been complete. Special thanks are due to Dr. Charles Brokopp, Utah Department of Health Laboratory, Division of Epidemiology and Laboratory Services, for his support for this study and his help on report preparation.

APPENDIX A

COLLABORATIVE STUDY PARTICIPANTS

APPENDIX A

COLLABORATIVE STUDY PARTICIPANTS

PARTICIPANTS AND PARAMETERS FOR THE JULY 13, 1998 PERCHLORATE IN WATER COLLABORATIVE STUDY	
Advanced Technology Laboratories Signal Hill, CA	AS-11:100mMol NaOH:1 mL/min:760 µL: Not listed:ASRS-4mm ext. water mode,6.2-7.32 min
Aerojet Environmental Laboratories Scaramento, CA	AS-5:120 mM NaOH+2 mM *p*-cyanophenol:1 mL/min:740 µL:5-100 ppb:AMMS II, 0.035 mM H2SO4, chemical suppression, recycle mode:start 6 min, finish 5.4 min
Alliant TechSystems Environmental Lab Magna, UT	FastSep:0.5920g NaOH+0.2382g 4-cyanophenol:1.4 mL/min:500 µL:5-100 ppb:AMM-I, 2.8 mL H2SO4/4L DI water, 4.2 mL/min:5.4 min
American Pacific Corporation - Utah Ops. Cedar City, Ut	AS-11:100 mMol NaOH:1000 µL:1 mL/min: 1 mL:5-200 ppb:ASRS Ultra autosuppression mode, 300 mA:8.9 min
Applied Research Associates, Inc. Tyndall AFB, FL	AS-11:100mMol NaOH:1 mL/min:760 µL:5-100 ppb:ASRS-4mm ext. water mode, 9 mL/min:6.9-7.3 min
Clayton Laboratory Services Novi, MI	AS-11:100mMol NaOH:1.6 mL/min:1000 µL:5-100 ppb:ASRS-II 4mm, 9 mL/min:6.9-7.3 min
Clinical Laboratory of San Bernardino San Bernardino, CA	AS-5:120 mM NaOH+2 mM *p*-cyanophenol: 0.7 mL/min:1000 µL:20 and 50 ppb:AMMS-II external mode:11.9 min
Department of Health Services Division of Drinking Water and Environmental Management Sanitation and Radiation Laboratories Branch Los Angeles, CA	AS 5:120 mM NaOH+2.0 mM *p*-cyanophenol:1 mL/min:750 µL:5-100 ppb:ASRS:7-7.5 min.
Dionex Applications Lab Sunnyvale, CA	AS-11:100 mMol NaOH:1 mL/min:1000 µL:5-100 ppb:ASRS Ultra, recycle mode:9.1 min
Edward S. Babcock & Sons, Inc. Riverside, CA	AS-5:120 mMol NaOH+2 mMol *p*-cyanophenol:1 mL/min:740 µL:4-250 ppb:Anion micromembrane suppressor:8.5 min

PARTICIPANTS AND PARAMETERS FOR THE JULY 13, 1998 PERCHLORATE IN WATER COLLABORATIVE STUDY	
Metropolitan Water District of Southern California La Verne, CA	AS-11:45 mMol NaOH+40% MeOH:1 mL/min:300 L:5-100 ppb:ASRS-II, chemical mode, power off:20 min at 5 % window
Montgomery Watson Laboratories Pasadena, CA	AS-11:100 mMol NaOH:1 mL:1 mL/min:1 mL:4-100 ppb:ASRS II, ext. water mode:9.4-10.3 min
Operational Toxicology Branch Human effectiveness Directorate Crew Survivability and Logisitics Division Wright-Patterson AFB, OH	AS-11:100 mMol NaOH:1 mL:1 mL/min:1 mL:Not reported:ASRS Ultra, ext. water mode,:6.9 – 0.6 min
Orange County Water District Fountain Valley, CA	AS-11:120mM NaOH:1 mL/min:750 µL:0-100 ppb:ASRS-II -4mm, 500 mA, ext. water mode, 5 mL/min:6.75 min
Southern Nevada Water System Boulder City, NV	AS-11:100mMol NaOH:1 mL/min:740 µL:0-24 ppb:ASRS Ultra, self regenerating:Not reported
State of Calif. Dept. of Health Services Sanitation & Radiation Laboratories North Berkeley, CA	AS-5:120 mM NaOH+2 mM *p*-cyanophenol:1 mL/min:740 µL:2.5-100 ppb:AMMS II, 75 mN H2SO4, 10 mL/min:7.3-7.5 min
Thiokol, Science and Engineering Brigham City, UT	AS-11:100 mMol NaOH:1 mL/min:1 mL:1-100 ppb:ASRS Ultra ext. water mode:Not reported
Utah Dept. of Health, Division of Epidemiology and Lab Services Salt Lake City, UT	AS-11:57 mM NaOH:1 mL/min:1000 µL:4-100 ppb:ASRS Ultra, outside water source:12.4 min
Weck Laboratories City of Industry, CA	AS-11:100mMol NaOH:1 mL/min:1 ml:5-1000 ppb:Dionex micro membrane:9 – 1 min

Legend- Column:eluent:eluent flow rate:sample size:standard range (minimum 5 standards):suppression parameters including acid concentration and flow rate:retention time of perchlorate peak

The matrix for all standards was DI water, and with the exception of Clinical Laboratory of San Bernardino, all laboratories used at least five standards for the calibration curve.

Totals: 13 AS-11, 5 AS-5, 1 AS-1.

APPENDIX B

MAJOR DISSOLVED CONSTITUENTS IN THE RAW WATER USED IN THE STUDY

Raw water (T3)	pH	Alk. As HCO3	TDS ppm	Si ppm	Cl^- ppm	$NO3^-$ ppm	$SO4^{2-}$ ppm	Ca^{++} ppm	K^+ ppm	Mg^{++} ppm	Na^+ ppm
C1T3 (1)	8.20-8.71	-	284-288	27.5	12.0-12.2	15.4-17.2	40.5-45	28-31	4.5-4.8	7.2-8.2	46.4-48.9
1997 (2)	7.72	168	-	30.0	11.1	15.7	37.6	24.0	5.40	7.40	51.0
7-31-90 (3)	8.12	159	-	28.1	11.8	-	40.9	26.4	5.26	8.21	48.9
9-11-90	8.13	158	-	28.5	11.4	-	41.2	24.7	5.34	8.18	48.1
1957-1990	8.10	159	-	-	11.6	-	41.0	25.6	5.30	8.20	48.5

Water T2 (50%)	pH	Alk. as HCO3	ppm TDS	ppm Si	ppm Cl	ppm NO3	ppm SO4	ppm Ca	ppm K	ppm Mg	ppm Na
C1T2	8.12-8.85	-	142-144	14.45	6.11	8.21	20.97	11.61	2.37	3.93	23.95

Water T1 (25%)	pH	Alk. as HCO3	ppm TDS	ppm Si	ppm Cl	ppm NO3	ppm SO4	ppm Ca	ppm K	ppm Mg	ppm Na
C1T2	7.93-8.80	-	71-72	10.10	3.25	8.21	10.22	6.06	1.22	1.97	12.59

ST0 Water	pH	Alk. as HCO3	ppm TDS	ppm Si	ppm Cl	ppm NO3	ppm SO4	ppm Ca	ppm K	ppm Mg	ppm Na
C1T2	7.60-7.80	-	-	1.12	0.36	0.15	0.10	0.26	0.00	0.01	2.60

(1) - Data provided by EERD(Ecological Exposure Research Division) - Cincinnati EPA, and cooperators 1K and 1N. TDS was determined by EPA Las Vegas RadQA and pH data was provided by the Air Force Research Laboratory, Toxicology Branch - Wright Patterson AFB.(2) Data from "UCRL-ID-130792, Hydrologic Resources Management Program and Underground Test Area Operable Unit FY 1997 Progress Report, Smith, D.K. et al May 1998". (3) Data from "DOE/NV/10845-16, Groundwater Chemistry at the Nevada Test Site: Data and Preliminary Interpretations, Chapman, J.B., and Lyles, B.F., March 1993"

APPENDIX C

INSTRUCTIONS TO PARTICIPANTS

Subject: Confirmation of participation in the perchlorate collaborative study.

Dear Name,

The purpose of this letter is to confirm your facilities intention to participate in the collaborative study of perchlorate methods. Before you commit, it is important that you understand the scope of the study, why it is necessary, and what you are asked to provide as a participant.

Included with this letter is a form listing your shipping address. Please verify that the address is correct and return via FAX (702-798-2236) to Steve Pia not later than July 2, 1997. Please keep the FAX transmission page as your receipt. This will acknowledge your commitment to participate. Your samples, lab code, and instructions will be sent on or about July 8, 1997, the study is scheduled to commence on July 13, 1997 and run until July 30, 1997. The drop dead date for data to be accepted is August 3, 1997.

Please accept my thanks for your participation. If you have any questions please contact Steve Pia at 702-798-2102 or by FAX at x2236.

Scope

The study encompasses only IC methods and includes only those laboratories which have produced data that has been used in the assessment and occurrence of perchlorate. Until recently the method of choice has been the CDHS method or simply the California protocol. It is this method compared to other IC variants that is the focus of the study. The laboratories addressed by this letter have been already been screened and all meet the criteria of previous experience.

The Necessity of a collaborative study

Detection of perchlorate in the water supplies of California, Nevada and Utah has generated intense interest during the last few months. Since so much was riding on the accuracy, precision, and implied specificity of the IC method, a collaborative study was inevitable. To date there simply has not been any data collected under controlled conditions so that both within and between laboratory variables could be evaluated. This study will answer a number of fundamental questions that will either reinforce confidence in the method, completely undermine that confidence, or identify some if not all of variables that may contribute to systematic error. The primary goal of this study is to assess within (repeatability) and between (reproducibility) laboratory variance, accuracy and bias.

Basic Study Design and Data Package Requirements

The study materials are composed of 13 samples prepared in well water known to be free from perchlorate. It may be of interest that the water is from a well located on the Nevada Test Site and was used in tritium performance evaluation samples because of the very low tritium background. If atomic blasts over the last 50 years have not contaminated the water it is unlikely that perchlorate will be present either. In addition to this presumption, verification of the samples will be conducted at the same time the study is being conducted.

Laboratory Analytical Requirements

(1) The samples will be analyzed in triplicate and in a specified sequence supplied with the samples. For this study the number of sample analyses will be 45 plus your routine calibration and QC samples.

(2) Laboratories are to run the sample batch only once and employing your typical calibration procedures and QC package. To the laboratory the samples should be processed like any routine sample batch.

(3) The laboratories will be asked to supply the follow data and information:

(a) the individual results
(b) copies of the all chromatograms for the samples, their calibration runs, and internal QC samples
(c) included with the chromatograms, participants are required to provide the raw data for all samples. Typically this information is part of the chromatogram.
(d) and the following specifications for the method employed:

(1) eluant, (2) flow rate, (3) column used, (4) manufacturer and model of the chromatograph. (5) data reduction by data processing software or integrator, (6) sample loop volume, (7) perchlorate salt used for standards and QC, (9) standard concentrations, (10) standard matrix, (11) type and model of pump (single or dual channel), (12) type of suppression, suppressor employed, and mode of operation, (13) make and model of detector used, and lastly (14) a run list or sample sequence report to help identify the order of analysis. A form will be provided with the samples to collect this information.

(4) It is anticipated that the analytical run will take 10-15 hours (45 samples, 15 cal. and QC, 10-15 minutes per sample) to complete in addition to the time required to set up the run. An additional day to assemble the various documents is also anticipated. Prepaid envelopes will be provide.

(5) Laboratories are requested to use the method with which they have generated the majority of data. This is particularly important if the data has been used in recent assessment or occurrence studies.

For those of you who participate, please accept the sincere thanks of the Analytical Subcommittee. Without your generous cooperation the collaborative would not be comprehensive, and it certainly could not have happened in such a short time period.

Sincerely,

Stephen Pia, Co-Chair
Analytical Subcommittee

INSTRUCTIONS

You have received 13 samples dated 28 June 1998, labeled C1 to 4, T1 to 3, and ST0 in glass containers. **Report any breakage or if you need more samples, call Steve Pia at 702-798-2102.** Please analyze the samples for perchlorate in the order stipulated below, record your results (g/L ClO4) on the enclosed report forms and fax the results to Steve Pia at 702-798-2236 as soon as possible but not later than **1200pm PDT 8/3/98.** Results received after that date will not be used in the study.

Time Table for Analysis and Data reporting:

Study start date: **7/13** or as soon as you received samples, please indicate the date and time you began the analysis.

Study stop date: **7/30/98**

Last day to submit results report forms: **1200pm PDT 8/3/98**

Last time to submit supplemental data: **Postmarked not later that 8/3/98**

Laboratory Analytical Requirements

(1) The samples are to be analyzed in triplicate and in a specified sequence following the table below. **Please..It is important that you follow the sequence in the table without any deviations. Please call me at 702-798-2102 if your laboratory can not follow the specified analytical sequence.** The sequence is such, that at the end of the run, all the study samples will have been analyzed in triplicate. For this study, the number of sample analyses will be 45 plus your routine calibration and QC samples.

ANALYTICAL SEQUENCE

First sequence:	Second sequence:	Third sequence:
C4T1, C4T2, C4T3, C1T1, ST0	C2T1, C3T1, C4T1, C1T1, ST0	C4T3, C3T3, C2T3, C1T3, ST0
C3T1, C3T2, C3T3, C1T2, ST0	C2T2, C4T2, C3T2, C1T2, ST0	C4T2, C3T2, C2T2, C1T2, ST0
C2T1, C2T2, C2T3, C1T3, ST0	C4T3, C3T3, C2T3, C1T3, ST0	C4T1, C3T1, C2T1, C1T1, ST0

(2) Laboratories are to run the sample batch, in the prescribed order, only once and employing your typical calibration procedures and QC package. To the laboratory, the samples should be processed like any routine sample batch. **Should a QC sample fail during the analysis, you are to follow your standard laboratory protocol for the re-analysis of samples following a failed QC sample.**

(3) The laboratories are asked to supply the following supplemental information postmarked **not later than 8/3/98:**

(a) the individual results, recorded on the enclosed report forms and faxed to 702-798-2236 as soon as practical after you have completed the analysis. Your replicate results are the central information of the study.

(b) copies of all the chromatograms for the samples, their calibration runs, and internal QC samples, postmarked not later than **8/3/98**. Data, reports, etc. dated after this date will not be included in the study. (If you encounter a problem during the analysis that may delay the submission of the entire data package beyond 8/3/98 please call me at 702-798-2102)

(c) included with the chromatograms, participants are asked to provide the raw data for all samples. Typically this information is part of the chromatogram.

(d) and the following specifications for the method employed (see enclosed method summary form):

(1) eluant, (2) flow rate, (3) column used, (4) manufacturer and model of the chromatograph, (5) data reduction process, software or integrator (eyeball and ruler works, too), please specify, (6) sample loop volume, (7) perchlorate salt used for standards and QC, (8) standard and QC sample concentrations, (9) standard matrix, (10) type and model of pump (single or dual channel), (11) type of suppression, suppressor employed, and mode of operation, (12) make and model of detector used, (13) a run list or sample sequence report to help identify the order of analysis, and lastly, (14) retention time of perchlorate peak. Forms will be provided with the samples to collect this information.

(4) It is anticipated that the analytical run will take 10-15 hours (45 samples, plus an estimated 15 calibration and QC sample package, and 10-15 minutes per sample) to complete in addition to the time required to set up the run. An additional day to assemble the various documents is also anticipated. Return addressed envelopes are provide (if you need more call me at 702-798-2102).

(5) Laboratories are requested to use the method with which they have generated the majority of data. This is particularly important if the data has been used in recent assessment or occurrence studies.

Any questions, please direct to **Steve Pia at 702-798-2102**. Thanks again for your participation. One final thought, you need to know that ALL the nation s qualified laboratories are participants in this study. In keeping with Ms. Browner s (Administrator of EPA, in case anyone forgot) priorities and emphasis on partnerships, this is a unique partnership and experience for all of us.

APPENDIX D

BLANK SAMPLE (C1T1,2,3)

9806 Perchlorate in Water collaborative study; collection date 28 June 1998

C1/T1 lab code	analysis 1	known value: expected precision: units: analysis 2	0 µg/L analysis 3
1A	0.7	-1	-1
1B	0	4.7	0
1C	<2.5	<2.5	<2.5
5D	-1	-1	-1
1E	0	0	0
1F	<5.0	<5.0	<5.0
1G	<4.0	<4.0	<4.0
5H	0	0	0
1I	0	0	0
1J	<4.0	<4.0	<4.0
1K	1.0	-1	-1
5L	-1	-1	-1
5M	<4.0	<4.0	<4.0
1N	0	0	0
2O	0	0	0
1P	<0.3	<0.3	<0.3
1Q	<4.0	<4.0	<4.0
1R	0	0	0
5S	<5.0	<5.0	<5.0

APPENDIX E

PERCHLORATE IN WATER COLLABORATIVE STUDY

JULY 13 SEPTEMBER 8, 1998

The following pages consist of separate sections for each of the sample types in this study with four parts per section. After the first, each part is separated from the next by a new page or a thick horizontal bar. The first page of each section is a statistical summary for the sample type and starts with a statement of the known value, the control limits, and the warning limits.

The warning limits are placed at two normalized standard deviations above and below the known value and the control limits are three normalized standard deviations above and below the known value. If you keep control charts, these values will be useful for anticipating problems with the accuracy of your analytical methods.

The coin shaped pie chart at the top of the summary page shows the fate of all the samples sent out in number and percentage terms. The pie chart starts at the top and rotates clockwise. The first sector represents those participants who submitted analytical results within both the warning and control limits. The next sector represents those who are in the warning region but not out of control. The third sector represents those who are out of control, but have passed the outlier test. The fourth sector represents those who have failed the outlier test. The last sector represents those participants who have failed to respond properly. This is the case if no analytical results were returned, or less than three determinations were reported, or if the results were received too late. The reeding on the edge of the coin is spaced at one percent intervals, and the sector shading becomes darker as the data reliability decreases. Sectors with zero width are not shown.

The table in the center shows a number of statistical quantities calculated from the submitted data based on the mean and median values in relation to the known value, both before and after outlier removal. The lower pie chart uses the same construction as the upper chart and shows the distribution of properly submitted data in terms of deviation from the known value divided into sectors representing one, two, three, and greater than three normalized standard deviations.

The second part is an alphabetical listing, in lab-code order, of submitted data and several calculated quantities. An entry that is shaded has been rejected because of one of the reasons listed above or failure of the outlier test. The fifth and sixth columns are a measure of laboratory precision. The Range analysis is a normalized value that you may use to keep precision control charts. The eighth and ninth columns are the differences from the mean of all non-outliers and from the known value, respectively. If this value is between 2.0 and 3.0, your analytical process precision is in the warning zone; if it exceeds 3.0 it is out of control. A tag symbol may appear in the last column. Each page with tags has a symbol definition summary at the bottom. If there is no tag symbol, the data is within the control limits, but it may be in the warning zone.

The third part is a three-column listing of result average, tag symbol, and lab-code in average order excluding those labs not responding properly. In this order, all outliers and out-of-control results appear at the top or bottom of the list.

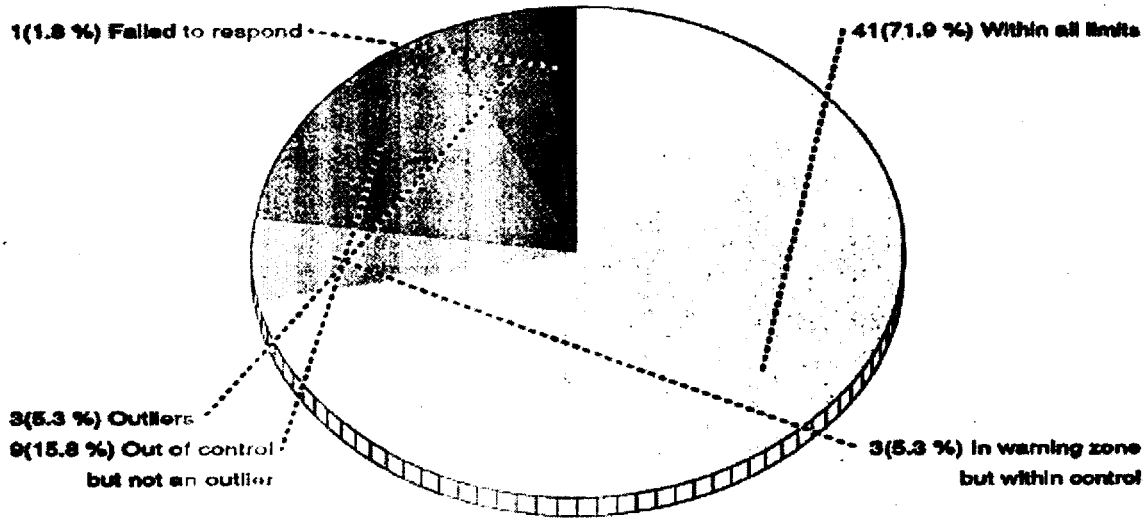
The last part is two bar chart displays showing frequency distributions of responding participants. The first chart places the known value at the center and a bar at each 0.2 unit of expected precision. The second chart places the mean of the reported measurements at the center and a bar at each 0.2 unit of standard deviation. In both cases, a bar includes those results within 0.1 unit up to the maximum of six. Any results more than six units from the center value are shown cumulatively by a shaded bar one past the sixth unit. If the central tendency of the known value distribution falls away from the center, an error in accuracy is indicated. If the distribution is broad, poor precision is indicated. The mean value distribution is similar but uses the average and standard deviation of reported results as its basis.

DRAFT

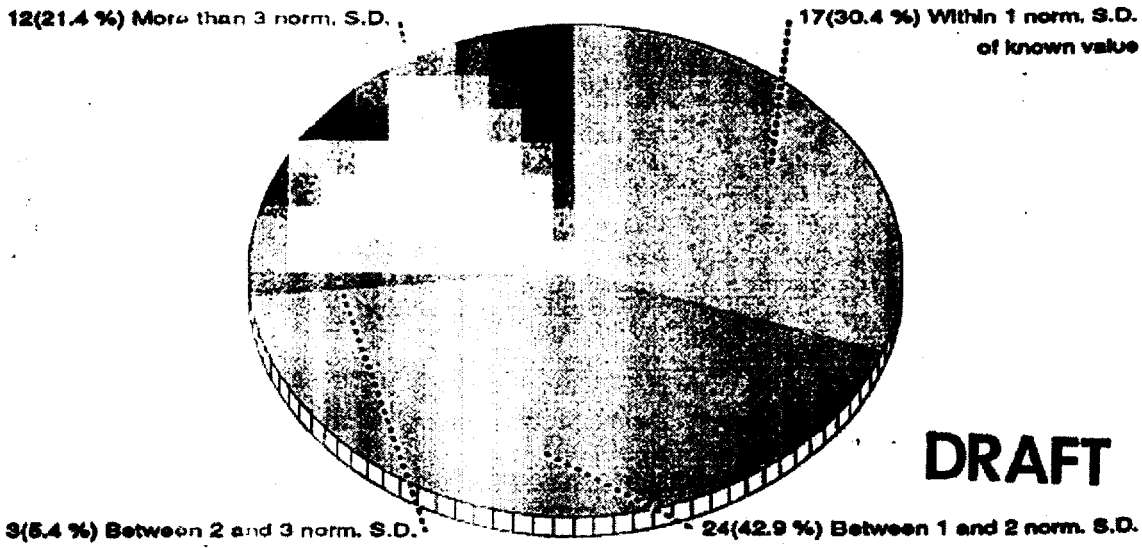
THIS PAGE INTENTIONALLY LEFT BLANK

S / T0 Statistical Summary **57 Participants**

The known value for this sample is **50.8** ug/L with an expected **precision of 2.2; the control limits are 47.0 to 54.6;** the warning **regions** are 47.0 to **48.3** and **53.3 to 54.6**



Statistic	Respondents	Non-outliers
Mean	51.79	Grand Avg 51.14
Std. Dev.	3.77	2.61
Variance	14.19	6.83
% Coef. of Var.	7.27	5.11
% deviation of mean from known value	1.95	0.66
Norm. dev. of mean from known value	0.26	0.13
Median	51.68	51.60
% deviation of median from known value	1.74	1.57
Norm. dev. of median from known value	0.23	0.31



DRAFT

4 / 33 ESD-LV **Collaborative** Study: **Perchlorate in Water, 13-Jul-1998**

S / T0

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	**49.0**	49.9	**48.5**	0.71	0.376	**49.13**	**-1.58**	**-1.31**	
1A	**52.0**	51.8	**50.6**	0.76	0.376	**51.47**	**0.26**	**0.52**	
1A	**48.9**	45.9	**48.8**	1.70	0.805	**47.87**	**-2.58**	**-2.31**	
1B	**48.6**	45.6	**52.7**	3.56	2.726	**48.97**	**-1.71**	**-1.44**	
1B	**49.6**	49.9	**47.9**	1.08	0.537	**49.13**	**-1.58**	**-1.31**	
1B	**47.3**	47.5	**44.2**	1.85	0.886	**46.33**	**-3.78**	**-3.52**	⇓
1C	**51.2**	51.1	**53.4**	1.30	0.618	**51.90**	**0.60**	**0.87**	
1C	**52.4**	54.7	**51.4**	1.69	0.886	**52.83**	**1.33**	**1.60**	
1C	**51.9**	53.0	**52.7**	0.57	0.295	**52.53**	**1.10**	**1.36**	
1E	**65.5**	62.1	**65.9**	2.09	1.039	**64.50**	**10.52**	**10.79**	×
1E	**64.9**	62.1	**61.1**	1.97	1.039	**62.70**	**8.10**	**8.37**	×
1E	**63.3**	60.6	**64.6**	2.04	1.141	**62.83**	**8.21**	**8.47**	×
1F	**53.2**	55.4	**55.7**	1.37	0.671	**54.77**	**2.86**	**3.12**	⇑
1F	**55.8**	56.4	**54.8**	0.81	0.430	**55.67**	**3.57**	**3.83**	⇑
1F	**53.5**	54.5	**53.1**	0.72	0.376	**53.70**	**2.02**	**2.28**	
1G	**52.6**	53.2	**52.9**	0.30	0.161	**52.90**	**1.39**	**1.65**	
1G	**51.9**	51.4	**52.4**	0.50	0.268	**51.90**	**0.60**	**0.87**	
1O	**53.4**	52.0							Ø
1I	**50.6**	51.4	**50.3**	0.57	0.295	**50.77**	**-0.29**	**-0.03**	
1I	**50.7**	50.6	**50.2**	0.26	0.134	**50.50**	**-0.50**	**-0.24**	
1I	**51.1**	50.3	**50.8**	0.40	0.215	**50.73**	**-0.32**	**-0.05**	
1J	**45.9**	44.5	**45.0**	0.71	0.376	**45.13**	**-4.73**	**-4.46**	⇓
1J	**43.6**	45.0	**44.9**	0.78	0.376	**44.50**	**-5.23**	**-4.96**	⇓
1J	**44.6**	44.6	**45.4**	0.46	0.215	**44.87**	**-4.94**	**-4.67**	⇓
1K	**49.8**	50.3	**50.4**	0.32	0.161	**50.17**	**-0.76**	**-0.50**	
1K	**51.2**	50.4	**50.6**	0.42	0.215	**50.73**	**-0.32**	**-0.05**	
1K	**52.1**	50.7	**49.6**	1.25	0.671	**50.80**	**-0.27**	**0.00**	
1N	**55.0**	54.7	**54.4**	0.30	0.161	**54.70**	**2.80**	**3.07**	⇑
1N	**55.5**	55.3	**56.3**	0.53	0.268	**55.70**	**3.59**	**3.86**	⇑
1N	**56.3**	56.7	**56.7**	0.23	0.107	**56.57**	**4.27**	**4.54**	⇑
1P	**52.7**	53.5	**51.3**	1.11	0.591	**52.50**	**1.07**	**1.34**	
1P	**53.3**	53.1	**52.8**	0.53	0.268	**52.90**	**1.39**	**1.65**	
1P	**51.5**	51.4	**52.8**	0.49	0.242	**51.73**	**0.47**	**0.73**	
1Q	**49.7**	48.0	**47.5**	1.15	0.591	**48.40**	**-2.16**	**-1.89**	
1Q	**47.6**	51.0	**47.7**	1.93	0.913	**48.77**	**-1.87**	**-1.60**	
1Q	**48.7**	49.2	**47.1**	1.10	0.564	**48.33**	**-2.21**	**-1.94**	
1R	**51.8**	52.7	**52.9**	0.59	0.295	**52.47**	**1.05**	**1.31**	
1R	**52.4**	52.4	**51.9**	0.29	0.134	**52.23**	**0.86**	**1.13**	
1R	**52.3**	52.7	**52.6**	0.21	0.107	**52.53**	**1.10**	**1.36**	
2O	**51.0**	49.5	**50.8**	0.81	0.403	**50.43**	**-0.55**	**-0.29**	
2O	**49.2**	51.2	**49.7**	1.04	0.537	**50.03**	**-0.87**	**-0.60**	
2O	**51.0**	51.9	**51.9**	0.52	0.242	**51.60**	**0.36**	**0.63**	
5D	**51.8**	52.6	**54.2**	1.22	0.644	**52.87**	**1.36**	**1.63**	
5D	**50.9**	55.1	**56.7**	3.00	2.061	**54.23**	**2.44**	**2.70**	
5D	**52.3**	52.9	**53.4**	0.55	0.295	**52.87**	**1.36**	**1.63**	

• = **No data** submitted

Ø = **Insufficient** data

TAG SYMBOLS

× = Determined to be an outlier

⇑ = Above control limit

⇓ = Below control limit

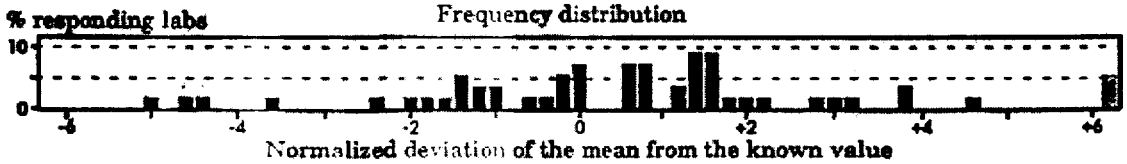
DRAFT

S / T0

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	Normalized deviation (known)	Tag
5H	51.2	50.6	50.1	0.55	0.295	50.63	-0.40	-0.13	
5H	49.4	52.7	57.8	4.23	3.391	53.30	1.70	1.97	
5H	53.4	54.3	47.0	3.98	2.828	51.57	0.34	0.60	
5L	50.2	48.9	49.2	0.68	0.349	49.43	-1.34	-1.08	
5L	48.8	49.4	49.4	0.35	0.161	49.20	-1.53	-1.26	
5L	48.8	49.6	49.9	0.57	0.295	49.43	-1.34	-1.08	
5M	50.9	52.3	52.1	0.76	0.376	51.77	0.50	0.76	
5M	47.7	49.2	50.6	1.45	0.779	49.17	-1.55	-1.29	
5M	52.4	52.5	50.0	1.42	0.671	51.63	0.39	0.66	
5S	51.0	51.0	56.0	2.89	1.652	52.67	1.20	1.47	
5S	52.0	55.0	50.0	2.52	1.652	52.33	0.94	1.21	
5S	53.0	55.0	51.0	2.00	1.141	53.00	1.47	1.73	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
44.50	⇓	1J	50.50		1I	52.53		1C
44.87	⇓	1J	50.63		5H	52.67		5S
45.13	⇓	1J	50.73		1K	52.83		1C
46.33	⇓	1B	50.73		1I	52.87		5D
47.87		1A	50.77		1I	52.87		5D
48.33		1Q	50.80		1K	52.90		1P
48.40		1Q	51.47		1A	52.90		1G
48.77		1Q	51.57		5H	53.00		5S
48.97		1B	51.60		2O	53.30		5H
49.13		1B	51.63		5M	53.70		1F
49.13		1A	51.73		1P	54.23		5D
49.17		5M	51.77		5M	54.70	⇑	1N
49.20		5L	51.90		1C	54.77	⇑	1F
49.43		5L	51.90		1G	55.67	⇑	1F
49.43		5L	52.23		1R	55.70	⇑	1N
50.03		2O	52.33		5S	56.57	⇑	1N
50.17		1K	52.47		1R	62.70	×	1E
50.43		2O	52.50		1P	62.83	×	1E
			52.53		1R	64.50	×	1E



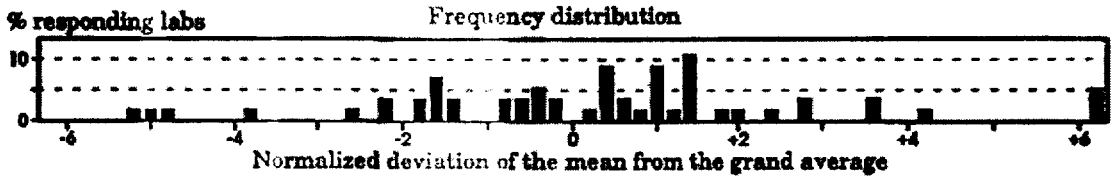
DRAFT

• = No data submitted
Ø = Insufficient data

TAG SYMBOLS
× = Determined to be an outlier

⇑ = Above control limit
⇓ = Below control limit

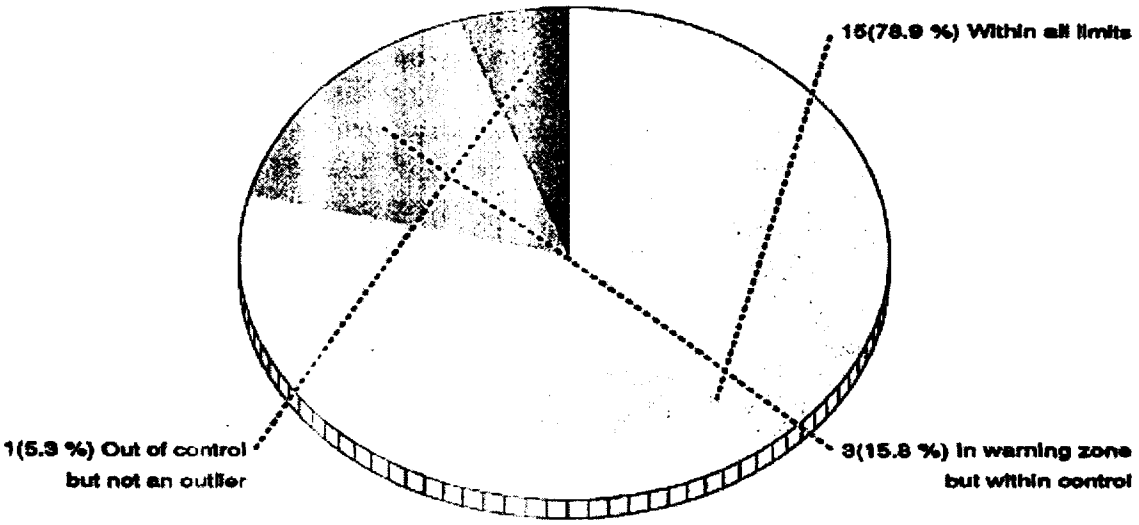
S / T0


% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

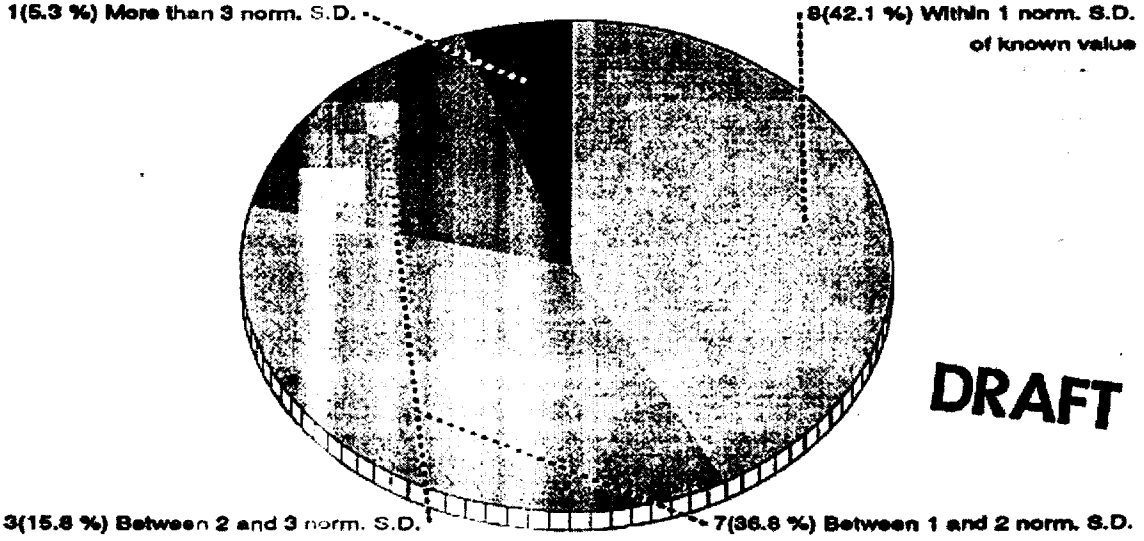
DRAFT

C2 / T1 Statistical Summary **19 Participants**

The known value for this sample is 5.8 ug/L with an expected precision of 0.8; the control limits are 4.4 to 7.2; the warning regions are 4.4 to 4.9 and 6.7 to 7.2



Statistic	Respondents	Non-outliers
Mean	5.66	**Grand Avg** 5.66
Std. Dev.	0.74	0.74
Variance	0.55	0.55
% Coef. of Var.	13.09	13.09
% deviation of mean from known value	-2.39	-2.39
Norm. dev. of mean from known value	-0.19	-0.19
Median	5.53	5.53
% deviation of median from known value	-4.60	-4.60
Norm. dev. of median from known value	-0.36	-0.36



DRAFT

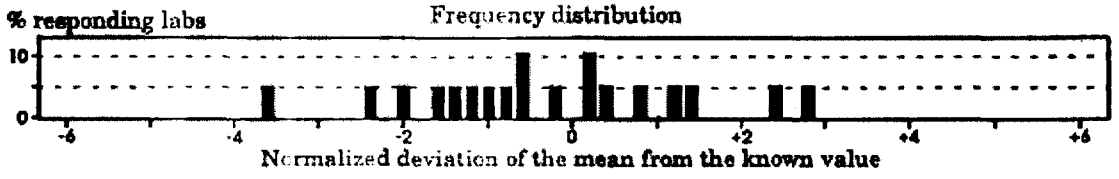
ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998

C2 / T1

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	Normalized deviation (known)	Tag
1A	5.0	6.0	6.2	0.64	0.886	5.73	0.16	-0.14	
1B	3.6	4.5	4.3	0.47	0.665	4.13	-3.31	-3.61	⇓
1C	5.3	5.1	5.1	0.12	0.148	5.17	-1.07	-1.37	
1E	5.2	5.3	5.3	0.06	0.074	5.27	-0.85	-1.15	
1F	7.4	6.2	7.6	0.76	1.064	7.07	3.04	2.74	
1G	5.4	5.0	6.0	0.50	0.738	5.47	-0.42	-0.72	
1I	5.1	5.1	5.1	0.00	0.000	5.10	-1.22	-1.52	
1J	4.6	4.9	5.2	0.30	0.443	4.90	-1.65	-1.95	
1K	5.3	5.4	5.3	0.06	0.074	5.33	-0.71	-1.01	
1N	6.0	6.5	6.7	0.36	0.517	6.40	1.60	1.30	
1P	5.9	6.5	6.9	0.50	0.738	6.43	1.67	1.37	
1Q	6.0	6.0	6.5	0.29	0.369	6.17	1.09	0.79	
1R	6.1	5.9	6.0	0.10	0.148	6.00	0.73	0.43	
2O	5.1	6.7	5.9	0.80	1.345	5.90	0.52	0.22	
5D	6.8	7.0	6.8	0.12	0.148	6.87	2.61	2.31	
5H	5.1	5.6	5.8	0.36	0.517	5.50	-0.35	-0.65	
5L	5.4	5.2	6.0	0.42	0.591	5.53	-0.28	-0.58	
5M	6.0	5.9	5.9	0.06	0.074	5.93	0.59	0.29	
5S	0.0	7.0	7.0	4.04	8.940	4.67	-2.15	-2.45	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
4.13	⇓	1B	5.33		1K	5.93		5M
4.67		5S	5.47		1G	6.00		1R
4.90		1J	5.50		5H	6.17		1Q
5.10		1I	5.53		5L	6.40		1N
5.17		1C	5.73		1A	6.43		1P
5.27		1E	5.90		2O	6.87		5D
						7.07		1F



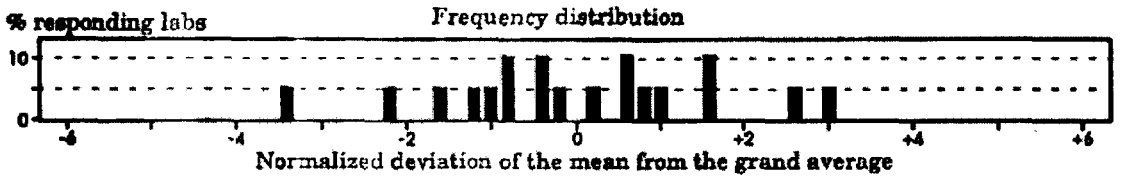
DRAFT

• = No data submitted
Ø = Insufficient data

TAG SYMBOLS
× = Determined to be an outlier

⇑ = Above control limit
⇓ = Below control limit

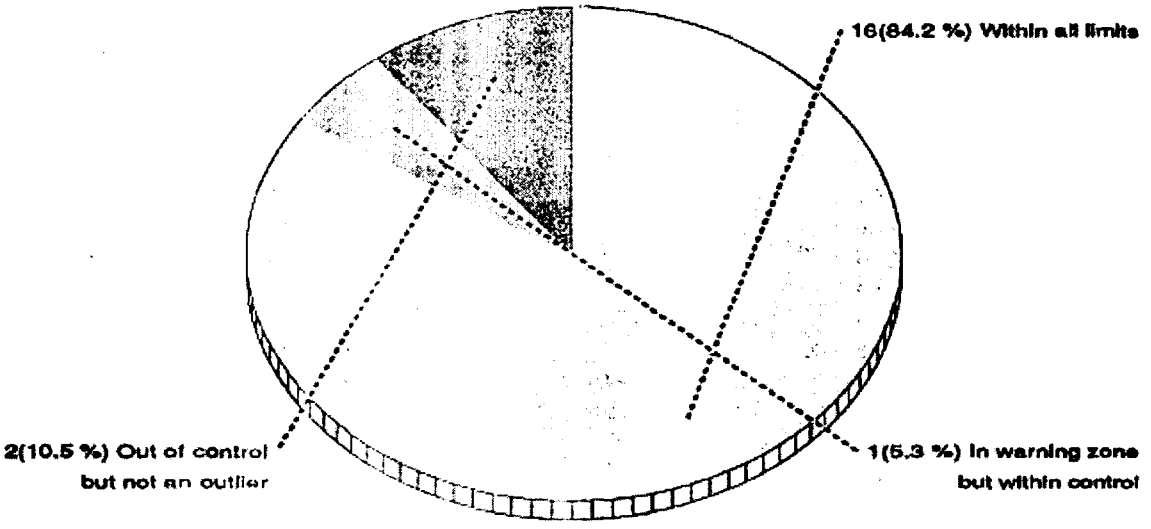
C2 / T1


% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

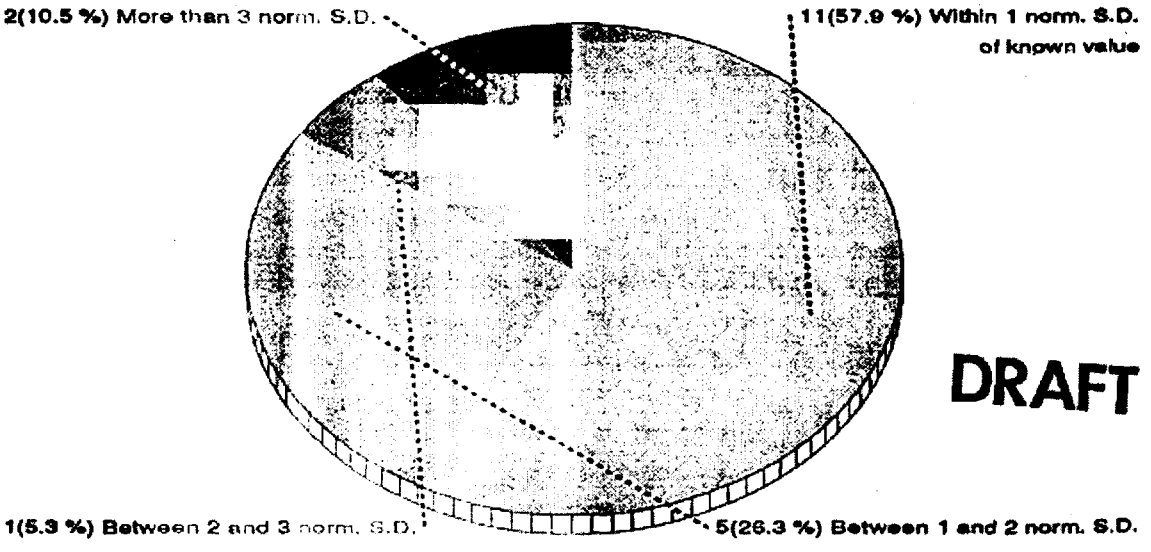
DRAFT

C3 / T1 Statistical Summary **19 Participants**

The known value for this sample is 17.9 ug/L with an expected precision of 1.6; the control limits are 15.1 to 20.7; the warning regions are 15.1 to 16.0 and 19.8 to 20.7



Statistic	Respondents	Non-outliers
Mean	17.96	**Grand Avg 17.98**
Std. Dev.	1.43	**1.43**
Variance	2.05	**2.05**
% Coef. of Var	7.97	**7.97**
% deviation of mean from known value	0.31	**0.31**
Norm. dev. of mean from known value	0.04	**0.04**
Median	17.87	**17.87**
% deviation of median from known value	-0.19	**-0.19**
Norm. dev. of median from known value	-0.02	**-0.02**



DRAFT

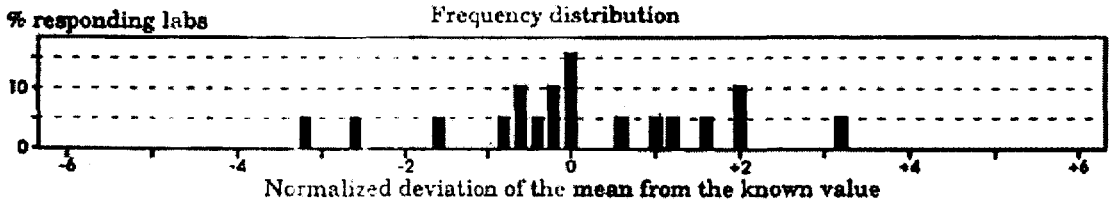
11 / 33 **ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998**

C3 / T1

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	17.5	18.4	17.1	0.67	0.480	17.67	-0.31	-0.25	
1B	15.4	16.2	14.9	0.66	0.480	15.50	-2.66	-2.60	
1C	17.4	17.4	19.0	0.92	0.591	17.93	-0.02	0.04	
1E	20.9	20.5	20.9	0.23	0.148	20.77	3.04	3.10	⇑
1F	19.3	18.4	20.2	0.90	0.665	19.30	1.45	1.52	
1G	17.1	18.3	17.3	0.64	0.443	17.57	-0.42	-0.36	
1I	14.9	14.9	14.9	0.01	0.000	14.90	-3.31	-3.25	⇓
1J	16.9	16.2	16.2	0.40	0.258	16.43	-1.65	-1.59	
1K	18.7	17.6	17.3	0.74	0.517	17.87	-0.10	-0.04	
1N	19.2	19.8	20.2	0.50	0.369	19.73	1.92	1.98	
1P	19.4	18.5	18.5	0.52	0.332	18.80	0.91	0.97	
1Q	17.0	17.3	17.4	0.21	0.148	17.23	-0.78	-0.72	
1R	18.3	18.5	18.5	0.12	0.074	18.43	0.52	0.58	
2O	17.9	18.3	17.5	0.40	0.295	17.90	-0.06	0.00	
5D	18.5	18.7	19.6	0.59	0.406	18.93	1.06	1.12	
5H	17.0	16.7	18.6	1.02	0.701	17.43	-0.57	-0.51	
5L	17.6	17.0	17.3	0.30	0.222	17.30	-0.71	-0.65	
5M	17.4	18.1	17.9	0.36	0.258	17.80	-0.17	-0.11	
5S	19.0	21.0	19.0	1.15	0.738	19.67	1.85	1.91	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
14.90	⇓	1I	17.57		1G	18.43		1R
15.50		1B	17.67		1A	18.80		1P
16.43		1J	17.80		5M	18.93		5D
17.23		1Q	17.87		1K	19.30		1F
17.30		5L	17.90		2O	19.67		5S
17.43		5H	17.93		1C	19.73		1N
						20.77	⇑	1E



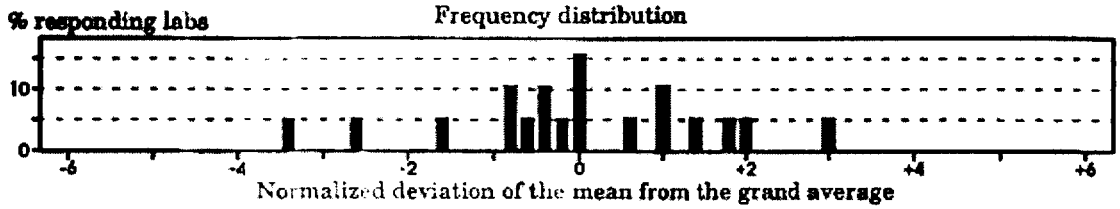
DRAFT

• = No data submitted
Ø = Insufficient data

TAG SYMBOLS
× = Determined to be an outlier

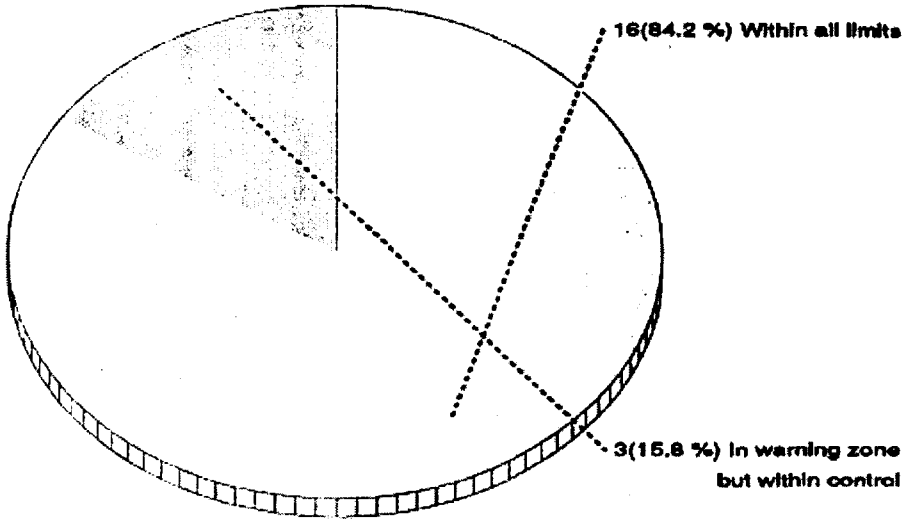
⇑ = Above control limit
⇓ = Below control limit

C3 / T1

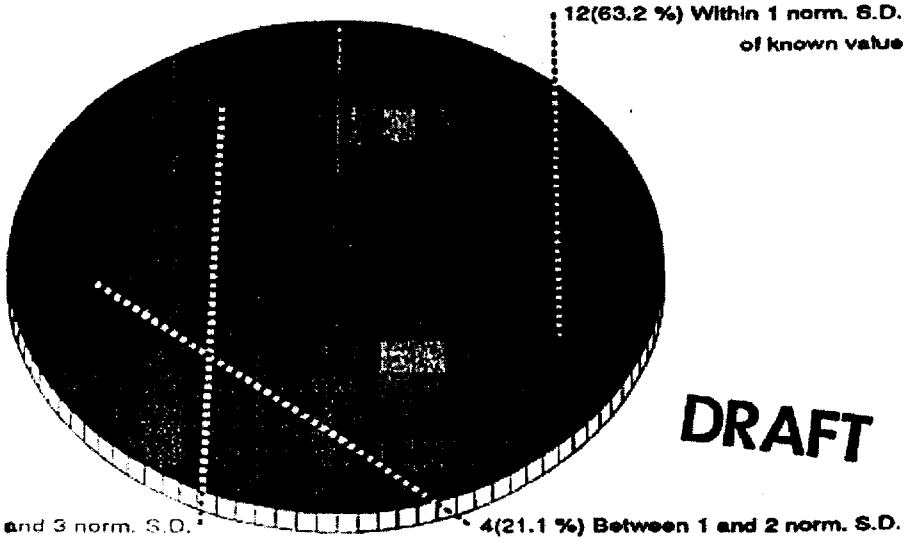

% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

C4 / T1 Statistical Summary **19 Participants**

The known value for this sample is 35.4 ug/L with an expected precision of **3.1; the control limits are 30.0 to 40.8**; the warning regions are 30.0 to 31.8 and 39.0 to 40.8



Statistic	Respondents	Non-outliers
Mean	34.99	**Grand Avg 34.99**
Std. Dev.	2.36	**2.36**
Variance	5.55	**5.55**
% Coef. of Var.	6.73	**6.73**
% deviation of mean from known value	-1.16	**-1.16**
Norm. dev. of mean from known value	-0.17	**-0.17**
Median	35.37	**35.37**
% deviation of median from known value	-0.09	**-0.09**
Norm. dev. of median from known value	-0.01	**-0.01**



DRAFT

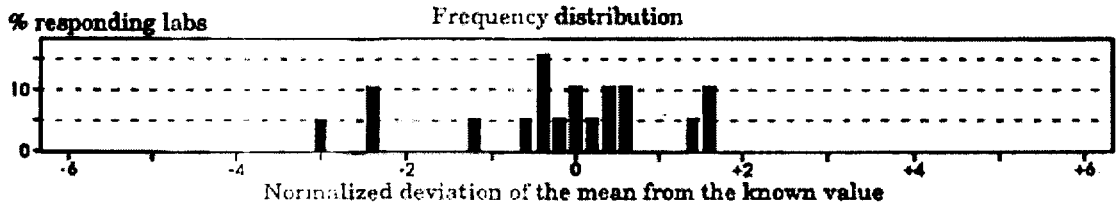
14 / 33 ESD-LV Collaborative Study: **Perchlorate in Water, 13-Jul-1998**

C4 / T1

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	**35.5**	35.5	34.5	0.68	**0.191**	**35.17**	**0.10**	**-0.13**	
1B	**30.5**	30.0	30.0	0.29	**0.095**	**30.17**	**-2.69**	**-2.92**	
1C	**33.9**	34.1	34.7	0.42	**0.152**	**34.23**	**-0.42**	**-0.65**	
1E	**32.0**	34.6	32.7	1.35	**0.495**	**33.10**	**-1.06**	**-1.29**	
1F	**37.2**	36.9	39.8	1.59	**0.553**	**37.97**	**1.66**	**1.43**	
1G	**36.0**	36.4	35.8	0.31	**0.114**	**36.07**	**0.60**	**0.37**	
1I	**31.4**	31.3	30.1	0.72	**0.248**	**30.93**	**-2.27**	**-2.50**	
1J	**31.6**	30.4	30.8	0.61	**0.229**	**30.93**	**-2.27**	**-2.50**	
1K	**36.3**	34.9	34.9	0.81	**0.267**	**35.37**	**0.21**	**-0.02**	
1N	**36.9**	38.5	39.8	1.45	**0.553**	**38.40**	**1.91**	**1.68**	
1P	**37.6**	34.5	36.0	1.55	**0.591**	**36.03**	**0.58**	**0.35**	
1Q	**36.2**	34.7	35.5	0.75	**0.286**	**35.47**	**0.27**	**0.04**	
1R	**36.7**	36.5	36.0	0.36	**0.133**	**36.40**	**0.79**	**0.56**	
2O	**34.3**	34.3	35.1	0.46	**0.152**	**34.57**	**-0.24**	**-0.47**	
5D	**35.2**	34.8	37.5	1.46	**0.514**	**35.83**	**0.47**	**0.24**	
5H	**33.7**	37.8	37.9	2.40	**0.800**	**36.47**	**0.83**	**0.60**	
5L	**35.6**	34.8	33.8	0.90	**0.343**	**34.73**	**-0.14**	**-0.37**	
5M	**33.3**	35.3	35.3	1.15	**0.381**	**34.63**	**-0.20**	**-0.43**	
5S	**35.0**	44.0	36.0	4.93	**2.362**	**38.33**	**1.87**	**1.64**	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
30.17		1B	34.63		**5M**	36.03		**1P**
30.93		1J	34.73		**5L**	36.07		**1G**
30.93		1I	35.17		**1A**	36.40		**1R**
33.10		1E	35.37		**1K**	36.47		**5H**
34.23		1C	35.47		**1Q**	37.97		**1F**
34.57		2O	35.83		**5D**	38.33		**5S**
						38.40		**1N**

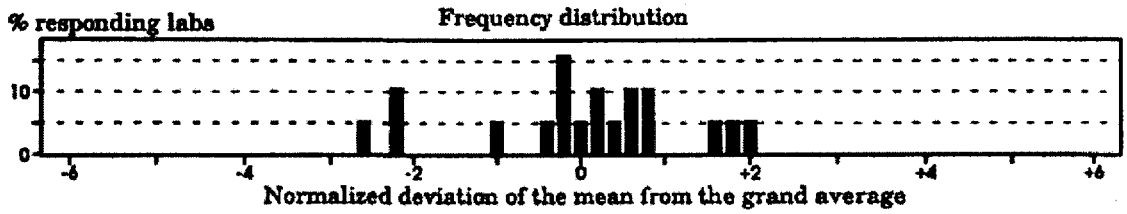


DRAFT

• = No data submitted | TAG SYMBOLS | ⇑ = Above control limit

Ø = Insufficient data | × = Determined to be an outlier | ⇓ = Below control limit

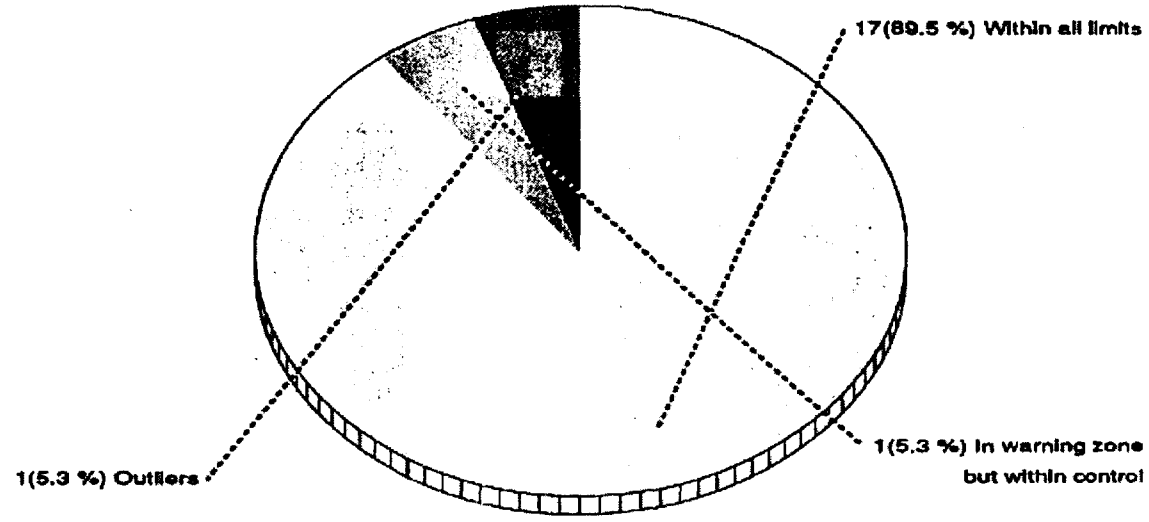
C4 / T1


% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

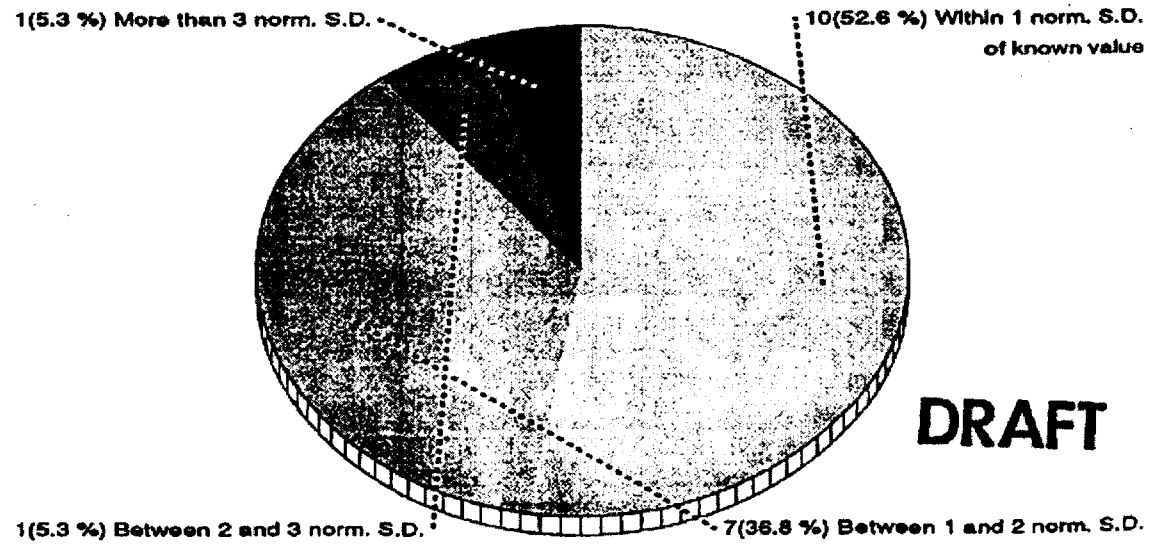
DRAFT

C2 / T2 Statistical Summary **19 Participants**

The known value for this sample is 5.8 ug/L with an expected precision of 0.8; the control limits are 4.4 to 7.2; the warning regions are 4.4 to 4.9 and 6.7 to 7.2



Statistic	Respondents	Non-outliers
Mean	5.69	Grand Avg 5.82
Std. Dev.	0.79	0.56
Variance	0.62	0.31
% Coef. of Var.	13.84	9.59
% deviation of mean from known value	-1.91	0.35
Norm. dev. of mean from known value	-0.14	0.04
Median	5.97	5.97
% deviation of median from known value	2.87	2.87
Norm. dev. of median from known value	0.21	0.30



DRAFT

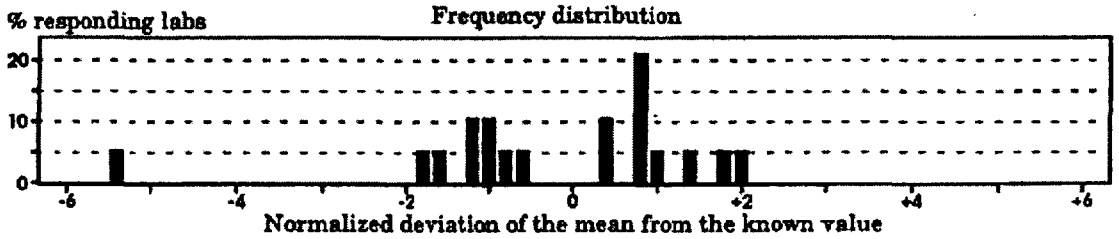
17 / 33 **ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998**

C2 / T2

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	Normalized deviation (known)	Tag
1A	6.3	5.8	5.8	0.29	0.369	5.97	0.32	0.36	
1B	4.0	5.4	6.8	1.40	3.033	5.40	-0.91	-0.87	
1C	5.7	5.0	5.4	0.35	0.517	5.37	-0.98	-0.94	
1E	5.3	5.1	5.5	0.20	0.295	5.30	-1.13	-1.08	
1F	6.1	5.8	6.6	0.40	0.591	6.17	0.75	0.79	
1G	5.3	5.1	5.2	0.10	0.148	5.20	-1.34	-1.30	
1I	5.1	5.0	5.1	0.06	0.074	5.07	-1.63	-1.59	
1J	5.3	4.5	5.2	0.44	0.591	5.00	-1.78	-1.73	
1K	5.6	5.5	5.4	0.10	0.148	5.50	-0.69	-0.65	
1N	6.6	6.6	7.0	0.23	0.295	6.73	1.98	2.02	
1P	6.7	6.4	6.8	0.21	0.295	6.63	1.76	1.80	
1Q	6.0	5.9	6.6	0.38	0.517	6.17	0.75	0.79	
1R	6.2	6.1	6.4	0.15	0.222	6.23	0.89	0.94	
2O	5.4	7.2	6.0	0.92	1.627	6.20	0.82	0.87	
5D	6.5	6.4	6.5	0.06	0.074	6.47	1.40	1.44	
5H	5.6	5.2	5.0	0.31	0.443	5.27	-1.20	-1.15	
5L	6.2	5.9	5.8	0.21	0.295	5.97	0.32	0.36	
5M	5.8	6.1	6.5	0.35	0.517	6.13	0.68	0.72	
5S	0.0	10.0	0.0	5.77	13.159	3.33	-5.38	-5.34	x

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
3.33	x	5S	5.37		1C	6.17		1Q
5.00		1J	5.40		1B	6.17		1F
5.07		1I	5.50		1K	6.20		2O
5.20		1G	5.97		5L	6.23		1R
5.27		5H	5.97		1A	6.47		5D
5.30		1E	6.13		5M	6.63		1P
						6.73		1N



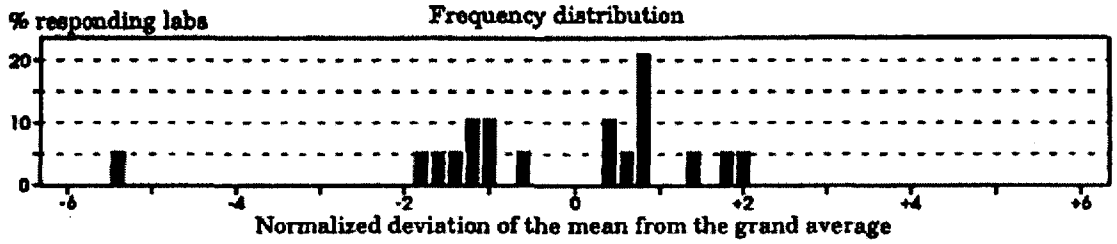
DRAFT

• ≡ No data submitted
Ø ≡ Insufficient data

TAG SYMBOLS
x ≡ Determined to be an outlier

⇑ ≡ Above control limit
⇓ ≡ Below control limit

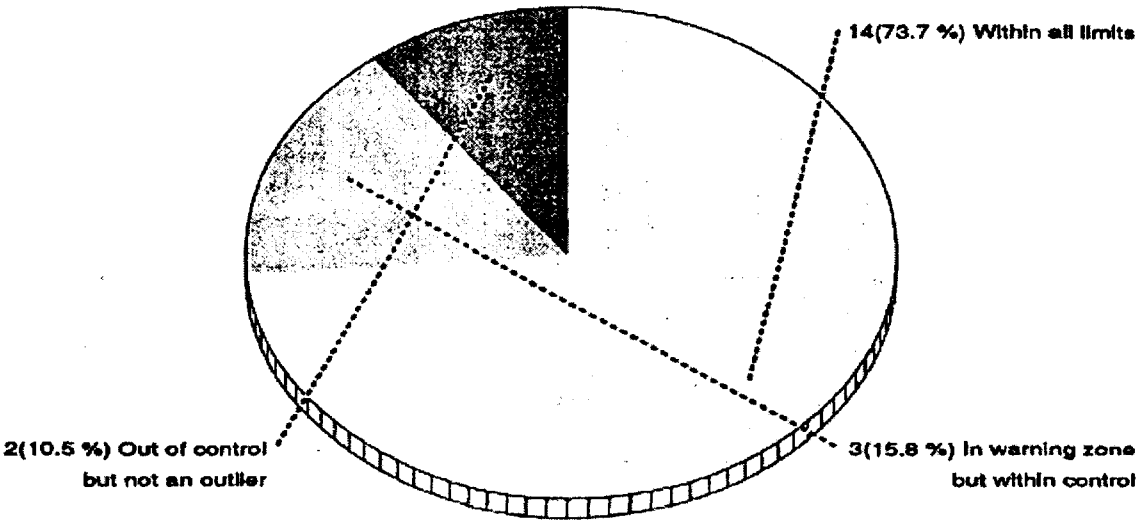
C2 / T2


% responding labs
Frequency distribution
20
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

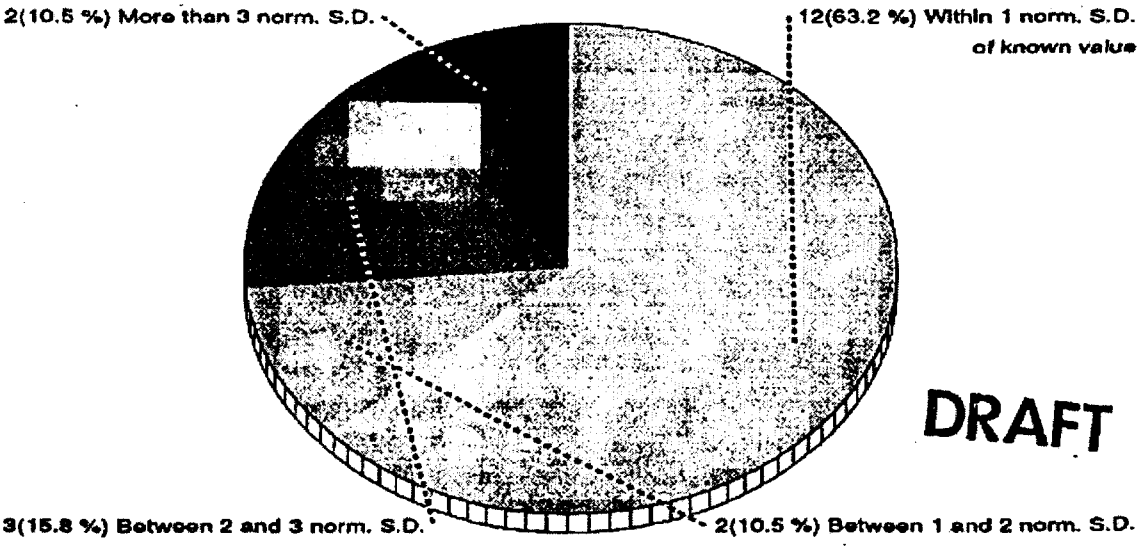
DRAFT

C3 / T2 Statistical Summary **19 Participants**

The known value for this sample is 17.9 ug/L with an expected precision of 1.6; the control limits are 15.1 to 20.7; the warning regions are 15.1 to 16.0 and 19.8 to 20.7



Statistic	Respondents	Non-outliers
Mean	17.79	Grand Avg 17.79
Std. Dev.	1.54	1.54
Variance	2.36	2.36
% Coef. of Var.	8.64	8.64
% deviation of mean from known value	-0.60	-0.60
Norm. dev. of mean from known value	-0.07	-0.07
Median	17.83	17.83
% deviation of median from known value	-0.37	-0.37
Norm. dev. of median from known value	-0.04	-0.04



DRAFT

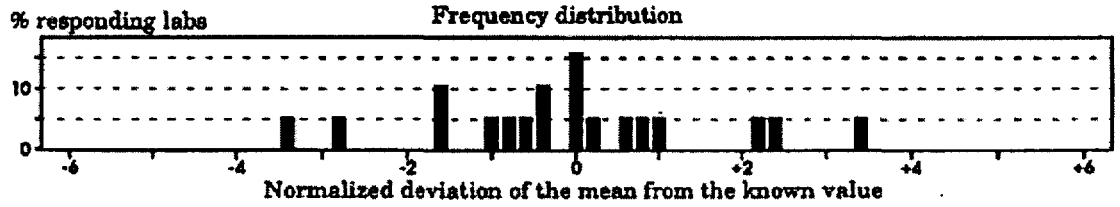
20 / 33 ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998

C3 / T2

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	17.3	16.8	17.2	0.26	0.185	17.10	-0.75	-0.87	
1B	15.0	15.7	15.0	0.40	0.258	15.23	-2.77	-2.89	
1C	16.8	17.5	17.6	0.44	0.295	17.30	-0.53	-0.65	
1E	17.8	17.5	18.5	0.51	0.369	17.93	0.15	0.04	
1F	20.1	19.3	20.7	0.70	0.517	20.03	2.43	2.31	
1G	17.4	18.3	17.8	0.45	0.332	17.83	0.04	-0.07	
1I	14.5	14.9	15.1	0.31	0.222	14.83	-3.20	-3.32	⇩
1J	15.8	16.1	17.4	0.85	0.591	16.43	-1.47	-1.59	
1K	17.6	17.5	17.4	0.10	0.074	17.50	-0.32	-0.43	
1N	19.5	19.9	20.5	0.50	0.369	19.97	2.35	2.24	
1P	18.5	18.8	18.7	0.15	0.111	18.67	0.95	0.83	
1Q	17.5	16.4	17.3	0.59	0.406	17.07	-0.79	-0.90	
1R	19.0	18.4	18.9	0.32	0.222	18.77	1.05	0.94	
2O	18.1	18.7	17.6	0.55	0.406	18.13	0.37	0.25	
5D	18.2	18.5	18.4	0.15	0.111	18.37	0.62	0.51	
5H	17.5	14.1	17.8	2.06	1.697	16.47	-1.44	-1.55	
5L	18.0	17.6	17.0	0.50	0.369	17.53	-0.28	-0.40	
5M	17.4	17.9	18.4	0.50	0.369	17.90	0.12	0.00	
5S	20.0	25.0	18.0	3.61	4.017	21.00	3.47	3.36	⇧

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
14.83	⇩	1I	17.30		1C	18.13		2O
15.23		1B	17.50		1K	18.37		5D
16.43		1J	17.53		5L	18.67		1P
16.47		5H	17.83		1G	18.77		1R
17.07		1Q	17.90		5M	19.97		1N
17.10		1A	17.93		1E	20.03		1F
						21.00	⇧	5S



DRAFT

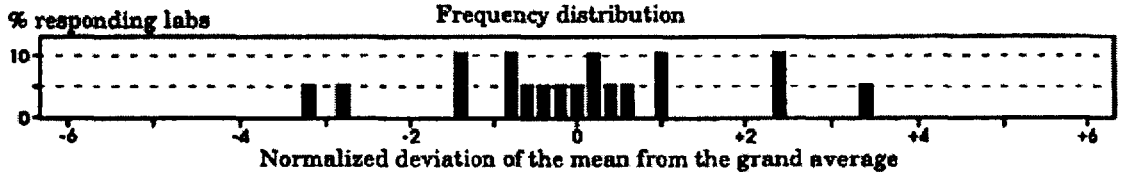
• = No data submitted
Ø = Insufficient data

TAG SYMBOLS

× = Determined to be an outlier

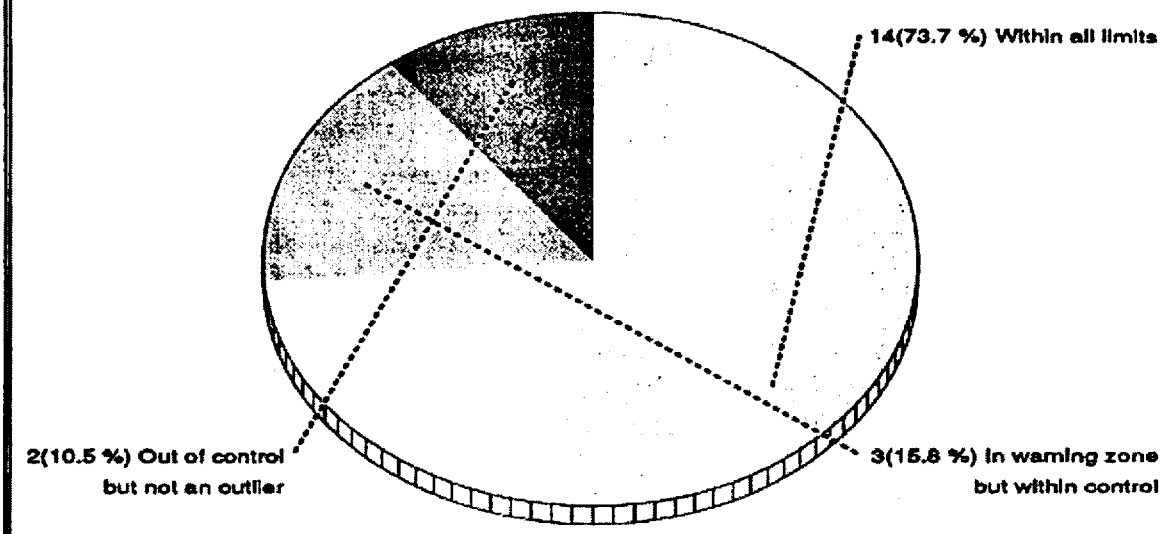
⇧ = Above control limit
⇩ = Below control limit

C3 / T2

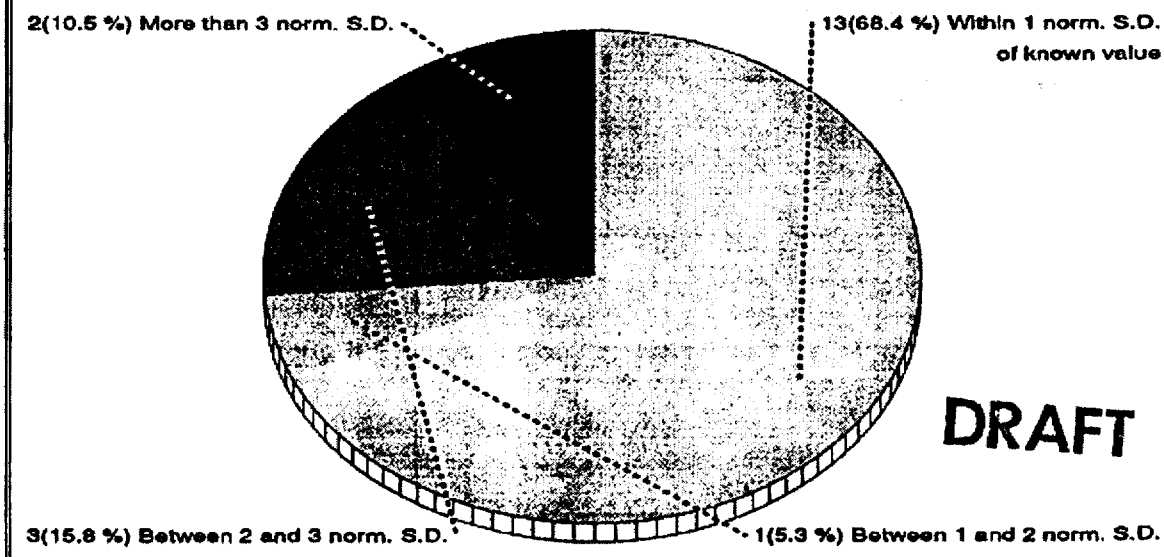

% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

C4 / T2 Statistical Summary 19 Participants

The known value for this sample is 36.1 ug/L with an expected precision of 3.1; the control limits are 30.7 to 41.5; the warning regions are 30.7 to 32.5 and 39.7 to 41.5



Statistic	Respondents	Non-outliers
Mean	35.50	Grand Avg 35.50
Std. Dev.	2.88	2.88
Variance	8.28	8.28
% Coef. of Var.	8.10	8.10
% deviation of mean from known value	-1.67	-1.67
Norm. dev. of mean from known value	-0.21	-0.21
Median	35.80	35.80
% deviation of median from known value	-0.83	-0.83
Norm. dev. of median from known value	-0.10	-0.10



DRAFT

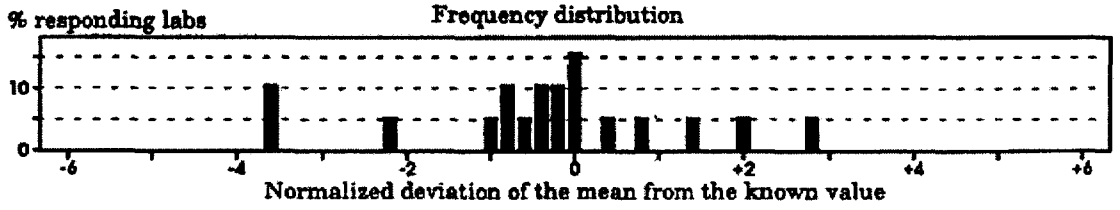
23 / 33 **ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998**

C4 / T2

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	36.1	34.4	34.4	0.98	0.324	34.97	-0.30	-0.63	
1B	31.2	24.6	33.2	4.50	2.216	29.67	-3.26	-3.59	⇓
1C	34.9	35.7	33.8	0.95	0.362	34.80	-0.39	-0.73	
1E	34.8	35.0	34.5	0.25	0.095	34.77	-0.41	-0.74	
1F	38.9	38.2	39.2	0.51	0.191	38.77	1.83	1.49	
1G	36.5	35.9	36.1	0.31	0.114	36.17	0.37	0.04	
1I	29.6	30.4	28.7	0.85	0.324	29.57	-3.31	-3.65	⇓
1J	31.8	32.4	32.5	0.38	0.133	32.23	-1.82	-2.16	
1K	36.4	35.7	35.8	0.38	0.133	35.97	0.26	-0.07	
1N	38.2	40.4	40.9	1.44	0.514	39.83	2.42	2.09	
1P	37.2	36.0	37.2	0.69	0.229	36.80	0.73	0.39	
1Q	35.2	34.8	33.0	1.17	0.419	34.33	-0.65	-0.99	
1R	37.7	37.0	37.6	0.38	0.133	37.43	1.08	0.74	
2O	35.9	35.8	36.3	0.50	0.191	35.80	0.17	-0.17	
5D	35.5	37.1	35.4	0.95	0.324	36.00	0.28	-0.06	
5H	37.7	35.9	34.0	1.85	0.705	35.87	0.21	-0.13	
5L	36.3	35.0	34.5	0.93	0.343	35.27	-0.13	-0.47	
5M	35.0	35.3	35.4	0.21	0.076	35.23	-0.15	-0.48	
5S	36.0	43.0	44.0	4.36	1.999	41.00	3.07	2.74	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
29.57	⇓	1I	34.97		1A	36.00		5D
29.67	⇓	1B	35.23		5M	36.17		1G
32.23		1J	35.27		5L	36.80		1P
34.33		1Q	35.80		2O	37.43		1R
34.77		1E	35.87		5H	38.77		1F
34.80		1C	35.97		1K	39.83		1N
						41.00		5S



DRAFT

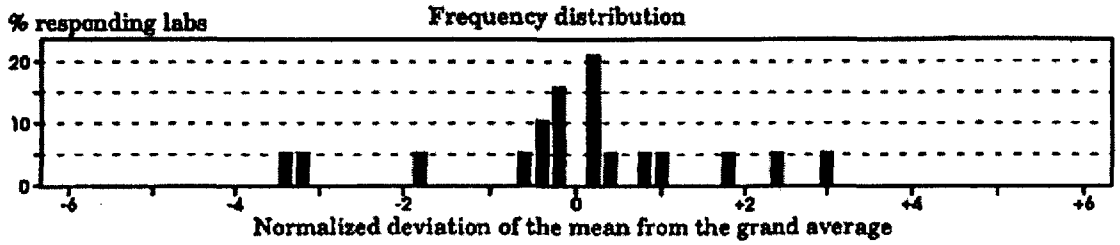
• = No data submitted
Ø = Insufficient data

TAG SYMBOLS

× = Determined to be an outlier

⇑ = Above control limit
⇓ = Below control limit

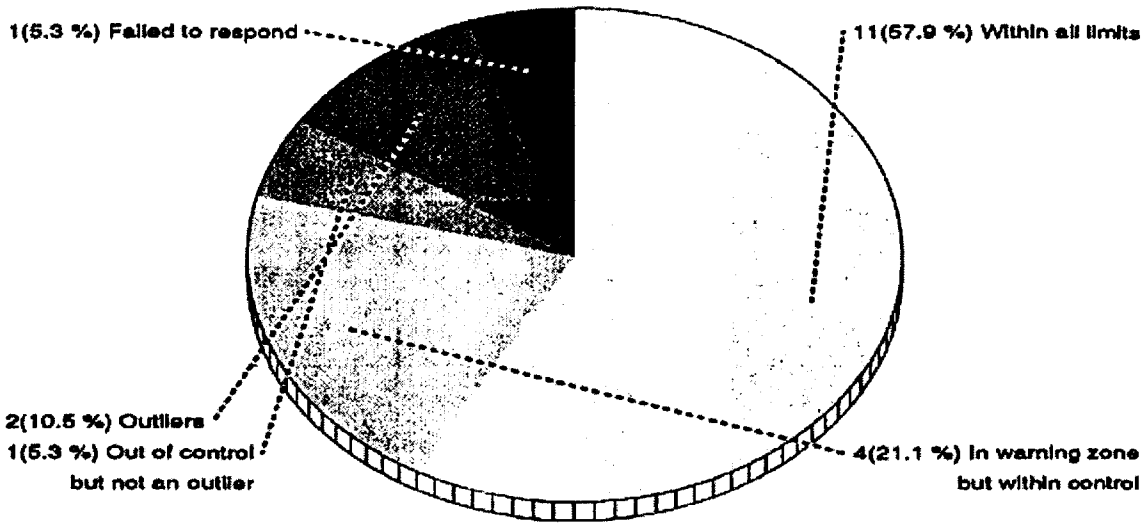
C4 / T2


% responding labs
Frequency distribution
20
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

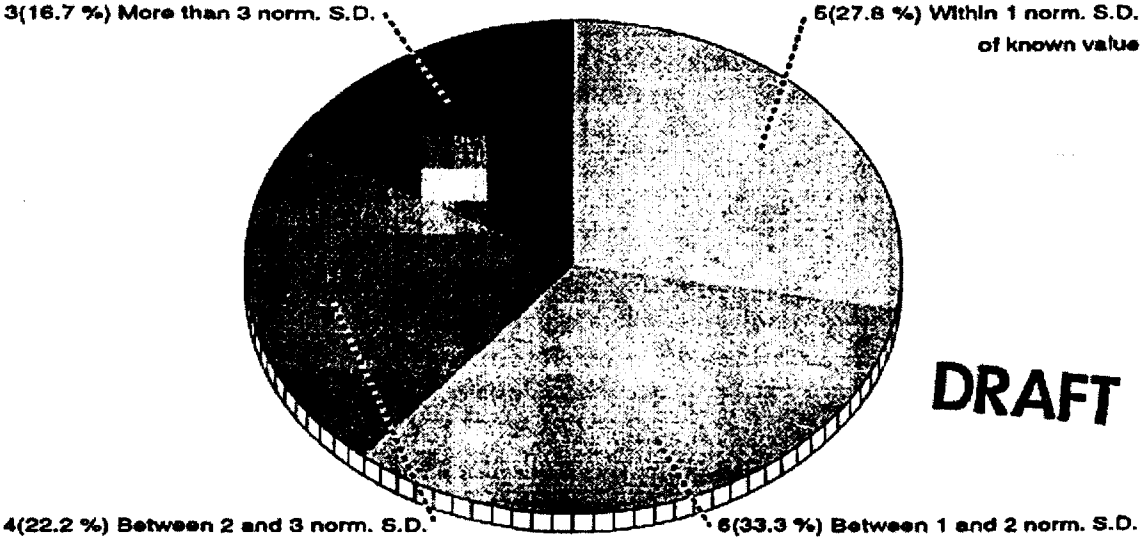
DRAFT

C2 / T3 Statistical Summary **19 Participants**

The known value for this sample is 5.8 ug/L with an expected precision of 0.8; the control limits are 4.4 to 7.2; the warning regions are 4.4 to 4.9 and 6.7 to 7.2



Statistic	Respondents	Non-outliers
Mean	5.96	Grand Avg 6.17
Std. Dev.	1.75	0.74
Variance	3.05	0.55
% Coef. of Var.	29.28	12.06
% deviation of mean from known value	2.81	6.32
Norm. dev. of mean from known value	0.09	0.49
Median	6.22	6.22
% deviation of median from known value	7.18	7.18
Norm. dev. of median from known value	0.24	0.56



DRAFT

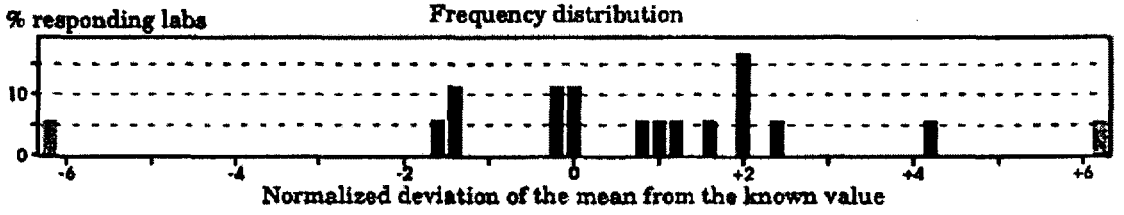
ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998

C2 / T3

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	Normalized deviation (known)	Tag
1A	5.9	7.9	6.5	1.03	1.908	6.77	1.30	2.09	
1B	9.5	5.1	8.7	2.34	5.283	7.77	3.46	4.26	⇑
1C	5.6	4.5	5.3	0.57	0.812	5.13	-2.24	-1.44	
1E	0.0	0.0	0.0	0.00	0.000	0.00	-13.35	-12.66	×
1F	6.1	6.8	7.3	0.60	0.886	6.73	1.23	2.02	
1G	5.4	6.1	5.6	0.36	0.517	5.70	-1.01	-0.22	
1I	5.1	5.1	5.1	0.00	0.000	5.10	-2.31	-1.52	
1J	5.3	4.8	5.4	0.32	0.443	5.17	-2.17	-1.37	
1K	5.9	5.7	5.9	0.12	0.148	5.83	-0.72	0.07	
1N	6.9	7.0	6.9	0.06	0.074	6.93	1.66	2.45	
1P	6.8	5.9	6.5	0.46	0.665	6.40	0.51	1.30	
1Q	6.1	6.0	6.4	0.21	0.295	6.17	0.00	0.79	
1R	6.6	6.7	6.3	0.21	0.295	6.53	0.79	1.59	
2O	6.4	7.5	6.3	0.67	0.886	6.73	1.23	2.02	
5D	8.3	9.4	8.3	0.64	0.812	8.67	5.41	6.21	×
5H	5.5	6.1	5.7	0.31	0.443	5.77	-0.87	-0.07	
5L	6.0	5.3	5.7	0.35	0.517	5.67	-1.08	-0.29	
5M	6.5	6.3	6.0	0.25	0.369	6.27	0.22	1.01	
5S	<5.0			9.0					Ø

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
0.00	×	1E	5.77		5H	6.73		2O
5.10		1I	5.83		1K	6.73		1F
5.13		1C	6.17		1Q	6.77		1A
5.17		1J	6.27		5M	6.93		1N
5.67		5L	6.40		1P	7.77	⇑	1B
5.70		1G	6.53		1R	8.67	×	5D



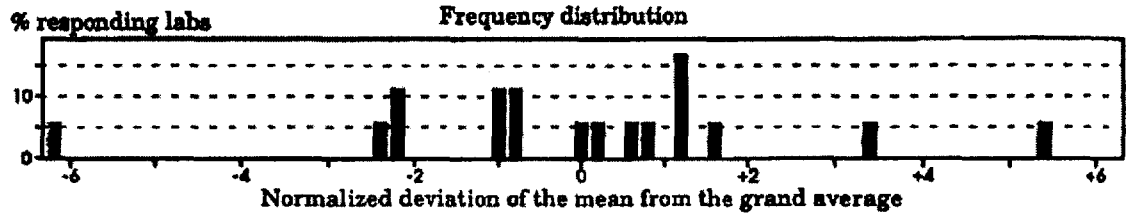
DRAFT

• = No data submitted
Ø = Insufficient data

TAG SYMBOLS
× = Determined to be an outlier

⇑ = Above control limit
⇓ = Below control limit

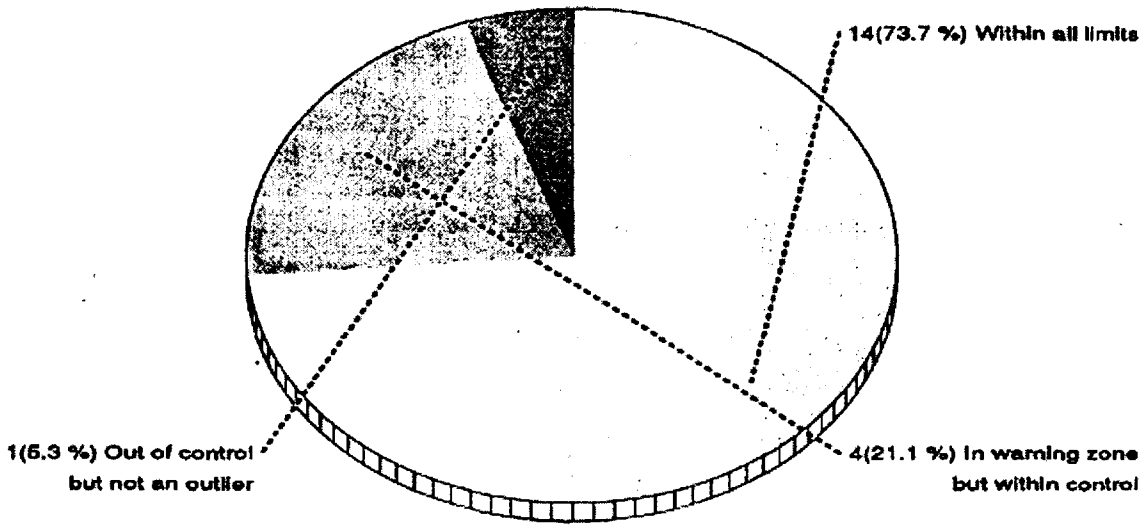
C2 / T3


% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

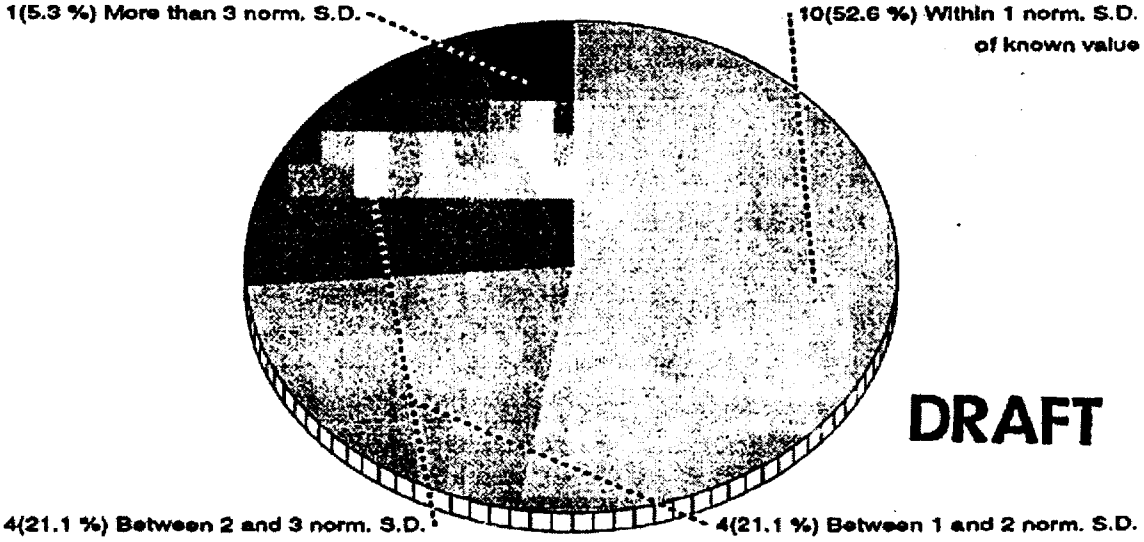
DRAFT

C3 / T3 **Statistical Summary** **19 Participants**

The known value for this sample is 17.9 ug/L with an expected precision of 1.6; the control limits are 15.1 to 20.7; the warning regions are 15.1 to 16.0 and 19.8 to 20.7



Statistic	Respondents	Non-outliers
Mean	17.87	Grand Avg 17.87
Std. Dev.	1.59	1.59
Variance	2.53	2.53
% Coef. of Var.	8.90	8.90
% deviation of mean from known value	-0.16	-0.16
Norm. dev. of mean from known value	-0.02	-0.02
Median	17.97	17.97
% deviation of median from known value	0.37	0.37
Norm. dev. of median from known value	0.04	0.04



DRAFT

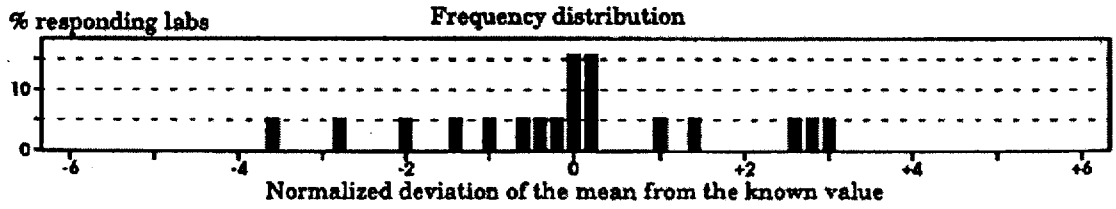
29 / 33 **ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998**

C3 / T3

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	17.3	18.8	17.1	0.93	0.628	17.73	-0.15	-0.18	
1B	15.8	15.2	14.9	0.46	0.332	15.30	-2.78	-2.81	
1C	16.8	17.1	16.8	0.17	0.111	16.90	-1.05	-1.08	
1E	18.3	17.6	18.0	0.35	0.258	17.97	0.10	0.07	
1F	20.1	19.8	20.8	0.51	0.369	20.23	2.56	2.53	
1G	17.7	18.2	18.5	0.40	0.295	18.13	0.28	0.25	
1I	14.4	14.8	14.8	0.23	0.148	14.67	-3.47	-3.50	⇩
1J	15.9	16.1	16.3	0.20	0.148	16.10	-1.92	-1.95	
1K	17.6	17.6	26.2	4.97	5.143	20.47	2.81	2.78	
1N	20.1	20.6	21.3	0.60	0.443	20.67	3.03	3.00	
1P	19.4	19.1	18.9	0.25	0.185	19.13	1.37	1.34	
1Q	17.1	17.8	16.9	0.47	0.332	17.27	-0.66	-0.69	
1R	18.3	18.9	19.1	0.42	0.295	18.77	0.97	0.94	
2O	18.7	18.1	17.5	0.60	0.443	18.10	0.25	0.22	
5D	19.1	18.7	16.3	1.51	1.064	18.03	0.17	0.14	
5H	18.2	18.3	17.4	0.49	0.332	17.97	0.10	0.07	
5L	17.9	17.8	17.1	0.44	0.295	17.60	-0.29	-0.32	
5M	17.1	18.3	18.2	0.67	0.443	17.87	-0.01	-0.04	
5S	11.0	19.0	20.0	4.93	5.424	16.67	-1.30	-1.34	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
14.67	⇩	1I	17.60		5L	18.10		2O
15.30		1B	17.73		1A	18.13		1G
16.10		1J	17.87		5M	18.77		1R
16.67		5S	17.97		5H	19.13		1P
16.90		1C	17.97		1E	20.23		1F
17.27		1Q	18.03		5D	20.47		1K
						20.67		1N

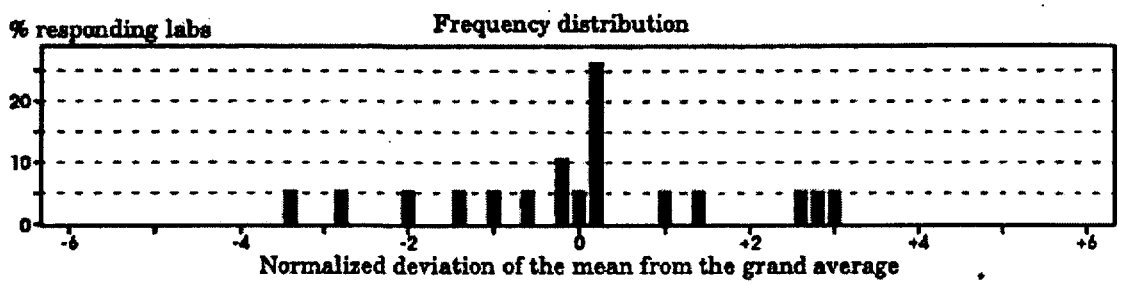


DRAFT

• = No data submitted | **TAG SYMBOLS** | ⇧ = Above control limit

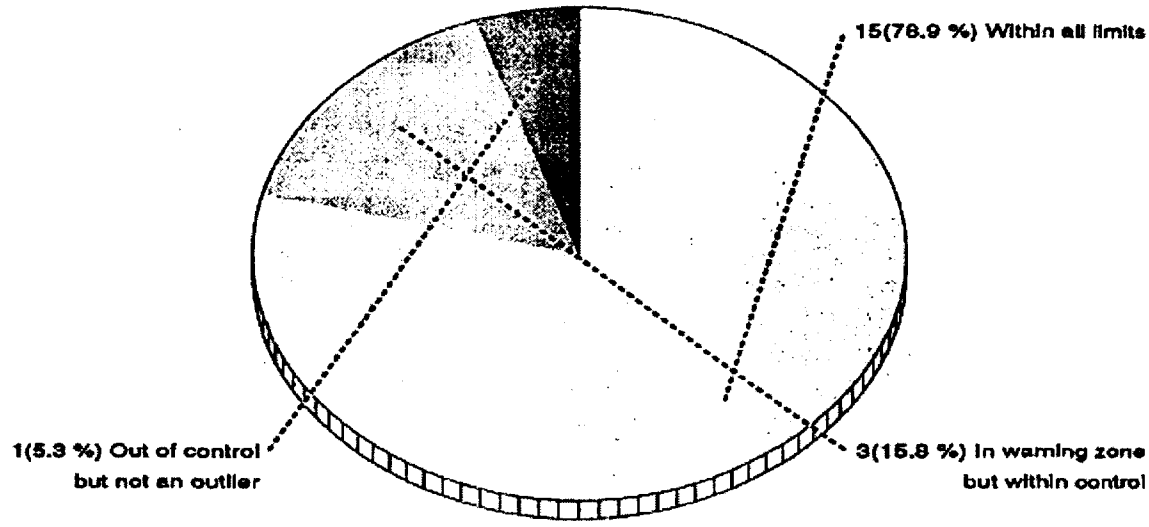
Ø = Insufficient data | × = Determined to be an outlier | ⇩ = Below control limit

C3 / T3

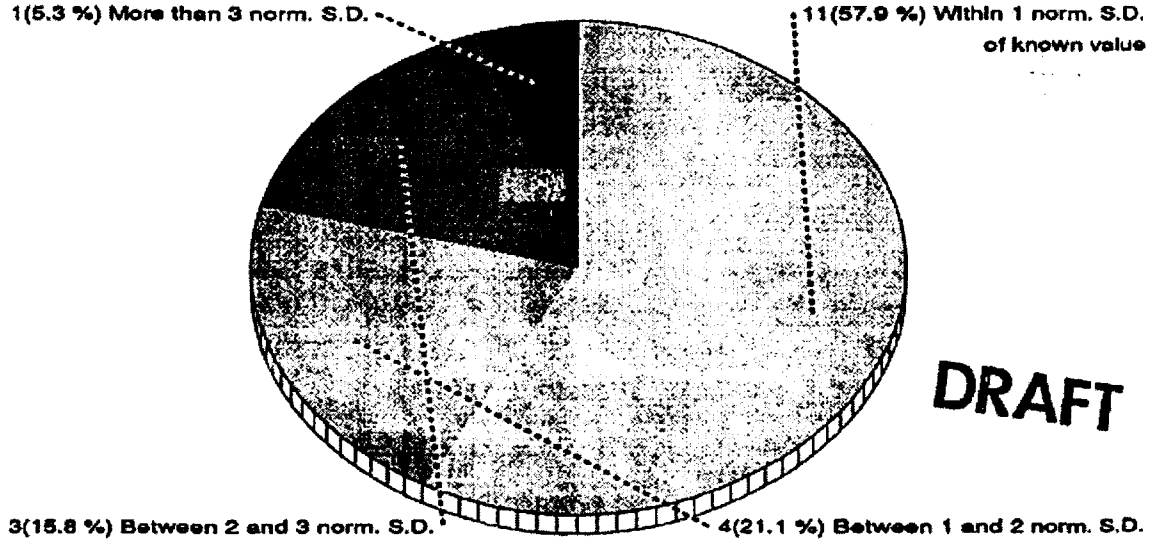

% responding labs
Frequency distribution
20
10
0
-6
-4
-2
0
+2
+4
+6
Normalized deviation of the mean from the grand average

C4 / T3 Statistical Summary **19 Participants**

The known value for this sample is 35.8 ug/L with an expected precision of 3.1; the control limits are 30.4 to 41.2; the warning regions are 30.4 to 32.2 and 39.4 to 41.2



Statistic	Respondents	Non-outliers
Mean	35.24	Grand Avg 35.24
Std. Dev.	2.80	2.80
Variance	7.85	7.85
% Coef. of Var.	7.95	7.95
% deviation of mean from known value	-1.57	-1.57
Norm. dev. of mean from known value	-0.20	-0.20
Median	35.27	35.27
% deviation of median from known value	-1.49	-1.49
Norm. dev. of median from known value	-0.19	-0.19



DRAFT

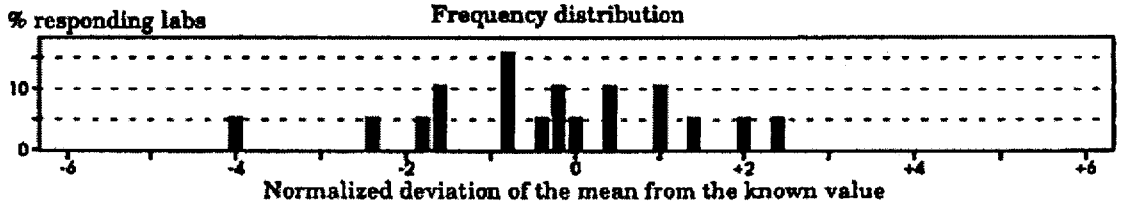
32 / 33 **ESD-LV Collaborative Study: Perchlorate in Water, 13-Jul-1998**

C4 / T3

Lab	Res. 1	Res. 2	Res. 3	Exper. Sigma	Rng anal (R + SR)	Average	Normalized deviation (grand-avg)	(known)	Tag
1A	35.9	35.0	34.9	0.55	0.191	35.27	0.02	-0.30	
1B	32.9	33.2	31.7	0.79	0.286	32.60	-1.47	-1.79	
1C	33.0	34.6	35.5	1.27	0.476	34.37	-0.49	-0.80	
1E	33.2	32.4	33.4	0.53	0.191	33.00	-1.25	-1.56	
1F	39.0	39.1	40.1	0.61	0.210	39.40	2.33	2.01	
1G	36.4	36.9	35.8	0.55	0.210	36.37	0.63	0.32	
1I	28.4	28.6	28.6	0.12	0.038	28.53	-3.75	-4.06	⇓
1J	31.4	33.0	30.4	1.31	0.495	31.60	-2.03	-2.35	
1K	35.4	35.6	35.8	0.20	0.076	35.60	0.20	-0.11	
1N	39.0	39.2	41.9	1.62	0.553	40.03	2.68	2.37	
1P	38.0	36.9	37.8	0.59	0.210	37.57	1.30	0.99	
1Q	34.1	34.2	35.1	0.55	0.191	34.47	-0.43	-0.74	
1R	37.8	37.3	37.4	0.26	0.095	37.50	1.26	0.95	
2O	35.1	37.2	34.9	1.27	0.438	35.73	0.28	-0.04	
5D	35.2	35.7	32.7	1.61	0.572	34.53	-0.39	-0.71	
5H	38.1	39.5	37.6	0.98	0.362	38.40	1.77	1.45	
5L	35.9	35.0	34.0	0.95	0.362	34.97	-0.15	-0.47	
5M	34.7	38.2	36.8	1.76	0.667	36.57	0.74	0.43	
5S	26.0	36.0	37.0	6.08	3.087	33.00	-1.25	-1.56	

Data sorted by Laboratory Average

Average	Tag	Lab	Average	Tag	Lab	Average	Tag	Lab
28.53	⇓	1I	34.47		1Q	36.37		1G
31.60		1J	34.53		5D	36.57		5M
32.60		1B	34.97		5L	37.50		1R
33.00		5S	35.27		1A	37.57		1P
33.00		1E	35.60		1K	38.40		5H
34.37		1C	35.73		2O	39.40		1F
						40.03		1N



DRAFT

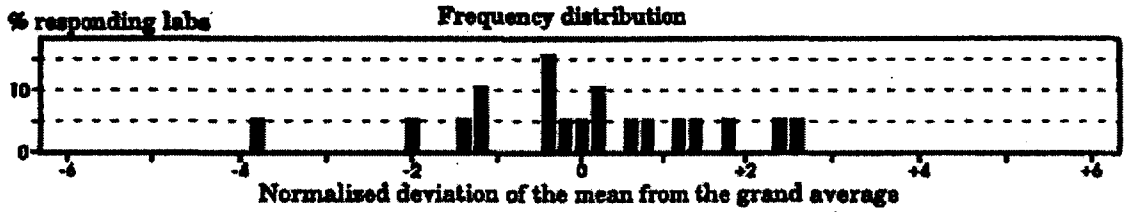
• = No data submitted
Ø = Insufficient data

TAG SYMBOLS

× = Determined to be an outlier

⇑ = Above control limit
⇓ = Below control limit

C4 / T3


% responding labs
Frequency distribution
10
0
-6
-4
-2
0
+2
+4
+6
Normalised deviation of the mean from the grand average

DRAFT

Yr	Mo	Prog	Con/TDS	Collection Date	Known value	Exp. prec.	Unit	Grand Avg.	1Sigma Labs	Norm. Dev.	Num Res	Num Acc	Num CL	%Lab inCL
98	6	PC01	S/T0	13-Jul-1998	50.8	2.20	ug/L	51.1	2.61	00.15	56	53	44	78.6
98	6	PC02	C1/T1	13-Jul-1998	0.0	0.10	ug/L	0.0	0.00	00.00	1	0	0	0.0
98	6	PC03	C2/T1	13-Jul-1998	5.8	0.80	ug/L	5.7	0.74	-00.17	19	19	18	94.7
98	6	PC04	C3/T1	13-Jul-1998	17.9	1.60	ug/L	18.0	1.43	00.03	19	19	17	89.5
98	6	PC05	C4/T1	13-Jul-1998	35.4	3.10	ug/L	35.0	2.36	-00.13	19	19	19	100.0
98	6	PC06	C1/T2	13-Jul-1998	0.0	0.10	ug/L	0.0	0.00	00.00	1	0	0	0.0
98	6	PC07	C2/T2	13-Jul-1998	5.8	0.80	ug/L	5.8	0.56	00.02	19	18	18	94.7
98	6	PC08	C3/T2	13-Jul-1998	17.9	1.60	ug/L	17.8	1.54	-00.07	19	19	17	89.5
98	6	PC09	C4/T2	13-Jul-1998	36.1	3.10	ug/L	35.5	2.88	-00.19	19	19	17	89.5
98	6	PC10	C1/T3	13-Jul-1998	0.0	0.10	ug/L	0.0	0.00	00.00	1	0	0	0.0
98	6	PC11	C2/T3	13-Jul-1998	5.8	0.80	ug/L	6.2	0.74	00.46	18	16	15	83.3
98	6	PC12	C3/T3	13-Jul-1998	17.9	1.60	ug/L	17.9	1.59	-00.02	19	19	18	94.7
98	6	PC13	C4/T3	13-Jul-1998	35.8	3.10	ug/L	35.2	2.80	-00.18	19	19	18	94.7

SAMPLE	G-avg Sx	Sr	SR	G-avg	KNOWN	ACC. %	BIAS	BIAS %
S/T0	2.61	1.55	2.90	51.1	50.8	100.6	0.30	0.59
C2/T1	0.74	0.42	0.82	5.7	5.8	98.3	-0.10	-1.72
C3/T1	1.43	0.66	1.53	18.0	17.9	100.6	0.10	0.56
C4T/1	2.36	1.56	2.68	35.0	35.4	98.9	-0.40	-1.13
C2/T2	0.56	0.47	0.68	5.8	5.8	100.0	0.00	0.00
C3/T2	1.54	0.68	1.63	17.8	17.9	99.4	-0.10	-0.56
C4/T2	2.88	1.35	3.08	35.5	36.1	98.3	-0.60	-1.66
C2/T3	0.74	0.46	0.84	6.2	5.8	106.9	0.40	6.90
C3/T3	1.59	1.75	2.14	17.9	17.9	100.0	0.00	0.00
C4/T3	2.80	1.74	3.14	35.2	35.8	98.3	-0.60	-1.68

VERIFICATION OF COLLABORATIVE SAMPLES IN GLASS BOTTLES - JULY 13,1998 STUDY SAMPLES

	C2	C3	C4	ST0
MEAN	6.27	17.9	34.5	53.9
SDV	0.35	0.90	2.15	0.00
MEAN	6.03	18.1	35.2	54.1
SDV	0.22	1.21	3.29	0.00
MEAN	6.58	18.0	35.3	50.1
SDV	0.32	1.31	3.24	3.10

	C2	C3	C4	ST0
MEAN	6.29	18.0	35.0	51.6
SDV	0.38	1.2	3.0	3.1
n	9	9	9	5
KWN VAL	5.83	17.86	35.37	50.77
% Rec	107.9	100.8	98.9	101.7
RPD	-7.6	-0.8	1.1	-1.7

Yr	Mo	Prog	Con/TDS	$S_{\bar{x}}$ Grand Std.dev.	#labs in CL	SDV labs in CL	#inCL Sig≠0	S_r SDV inCL Sig≠0	# of SDV=0	% of SDV=0	S_L	S_R
98	6	PC01	S/T0	2.61	44	1.55	44	1.55	0	0.0	2.46	2.90
98	6	PC02	C1/T1									
98	6	PC03	C2/T1	0.74	17	0.40	16	0.42	1	5.9	0.70	0.82
98	6	PC04	C3/T1	1.43	17	0.66	17	0.66	0	0.0	1.38	1.53
98	6	PC05	C4/T1	2.36	19	1.56	19	1.56	0	0.0	2.18	2.68
98	6	PC06	C1/T2									
98	6	PC07	C2/T2	0.56	18	0.47	18	0.47	0	0.0	0.49	0.68
98	6	PC08	C3/T2	1.54	17	0.68	17	0.68	0	0.0	1.49	1.63
98	6	PC09	C4/T2	2.88	17	1.35	17	1.35	0	0.0	2.77	3.08
98	6	PC10	C1/T3									
98	6	PC11	C2/T3	0.74	15	0.45	14	0.46	1	6.7	0.69	0.84
98	6	PC12	C3/T3	1.59	18	1.75	18	1.75	0	0.0	1.23	2.14
98	6	PC13	C4/T3	2.80	18	1.74	18	1.74	0	0.0	2.61	3.14

APPENDIX F

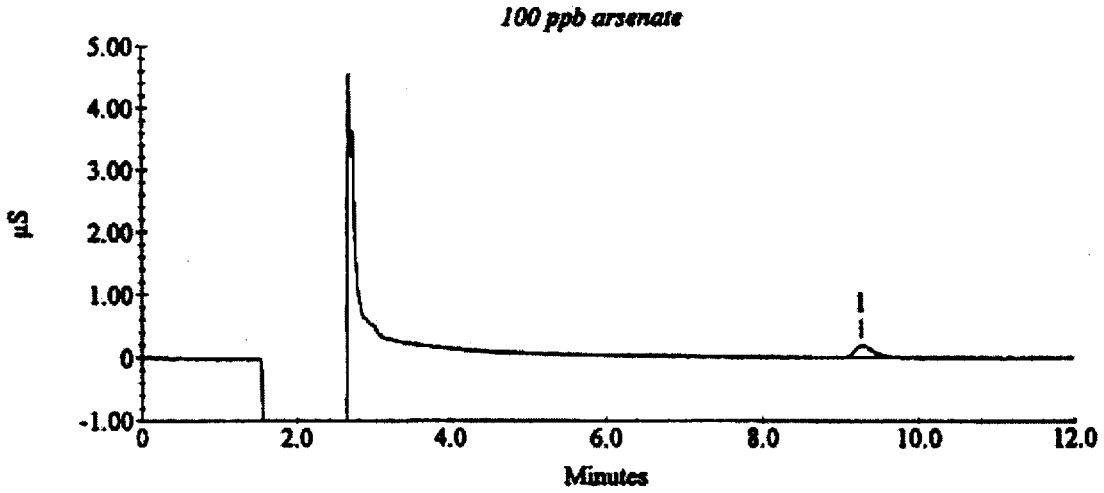
ION CHROMATOGRAMS

ANION INTERFERENCE STUDY

100 ppb Arsenate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

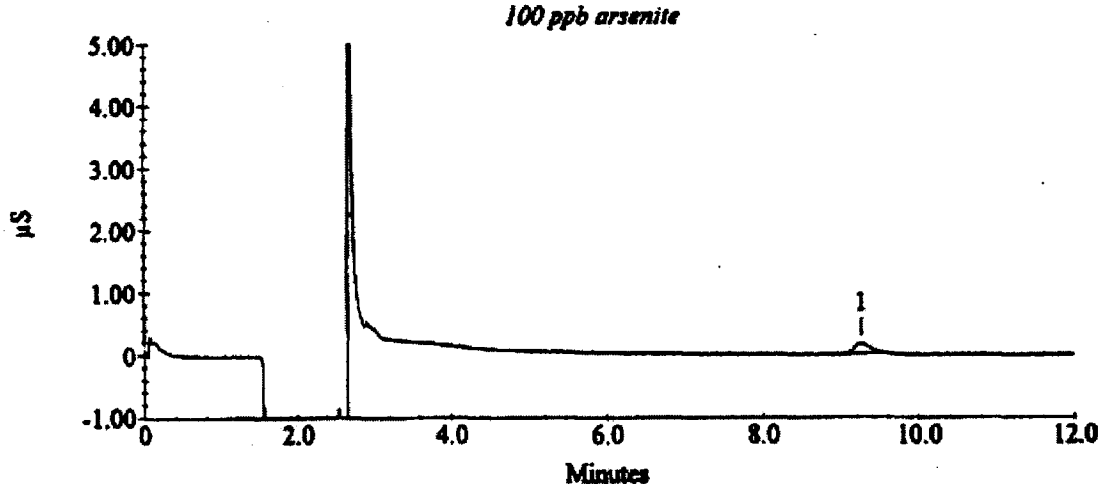
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.27	0.00	29375	1826



100 ppb arsenite in the presence of 20 ppb perchlorate

Peak Information : All Peaks

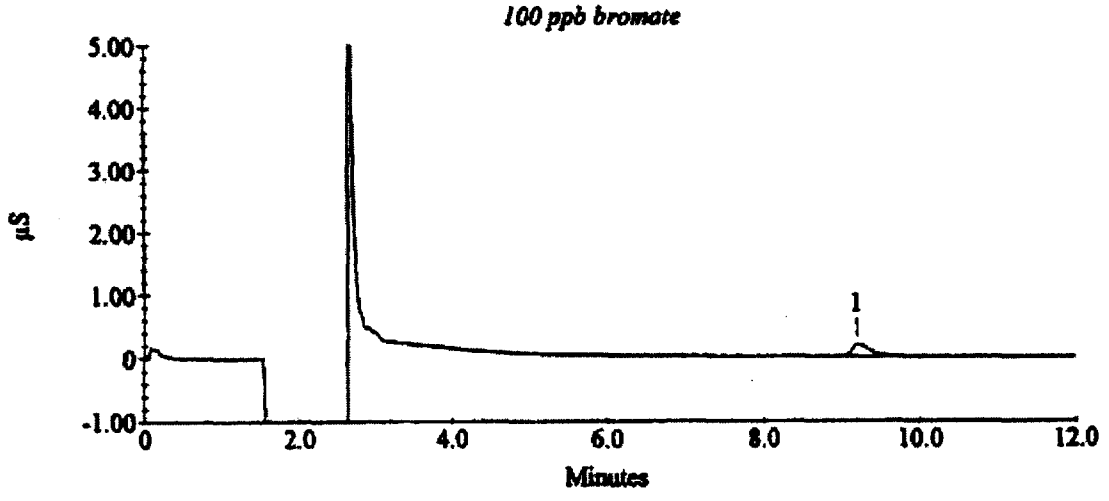
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.27	0.00	21750	1510



100 ppb bromate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

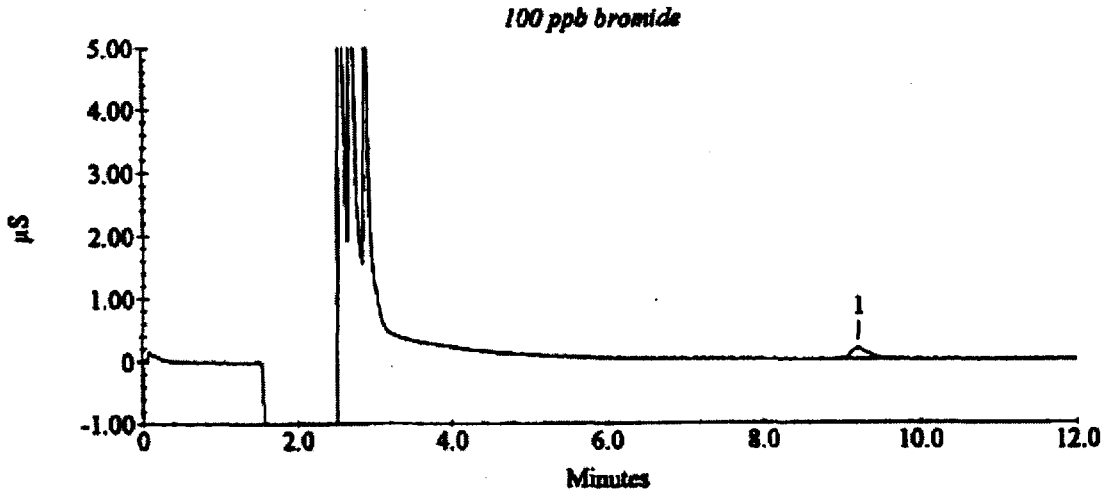
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.20	0.00	31046	1780



100 ppb bromide in the presence of 20 ppb perchlorate

Peak Information : All Peaks

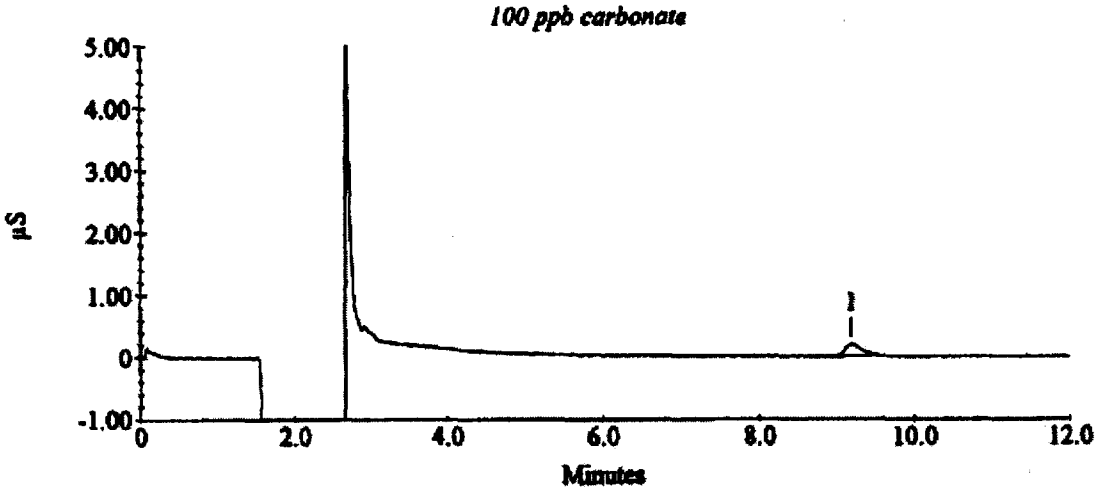
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.22	0.00	25618	1715



100 ppb carbonate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

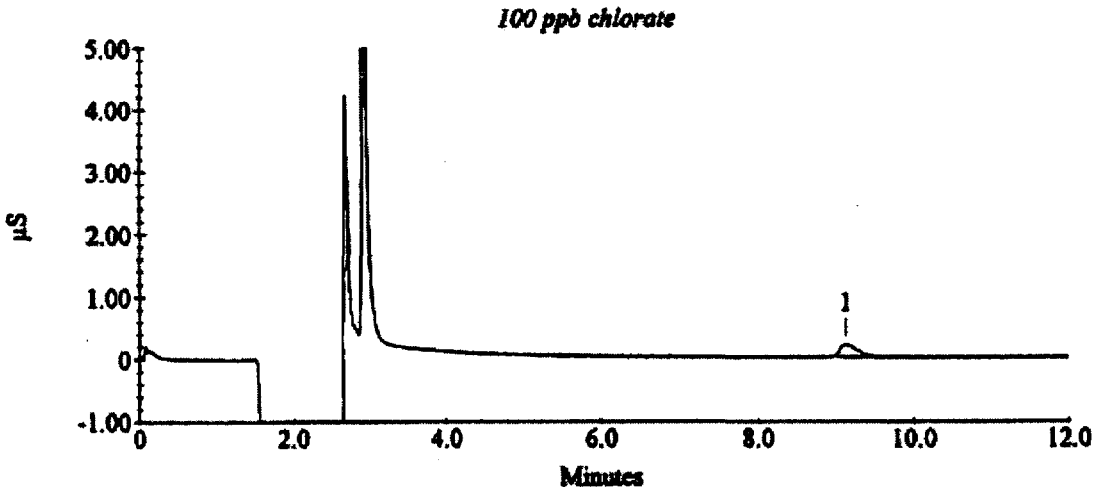
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.18	0.00	28979	1959



100 ppb chlorate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

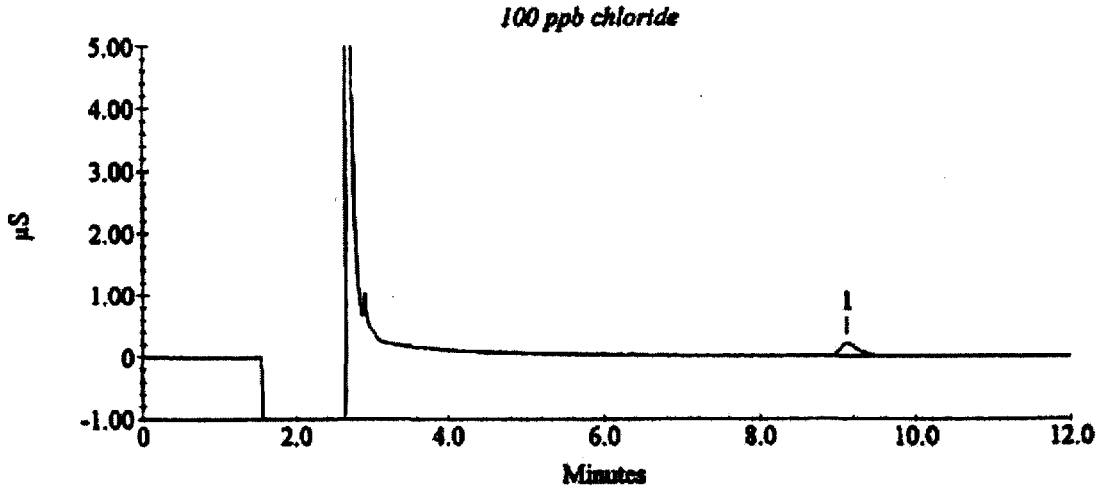
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.13	0.00	30649	2015



100 ppb chloride in the presence of 20 ppb perchlorate

Peak Information : All Peaks

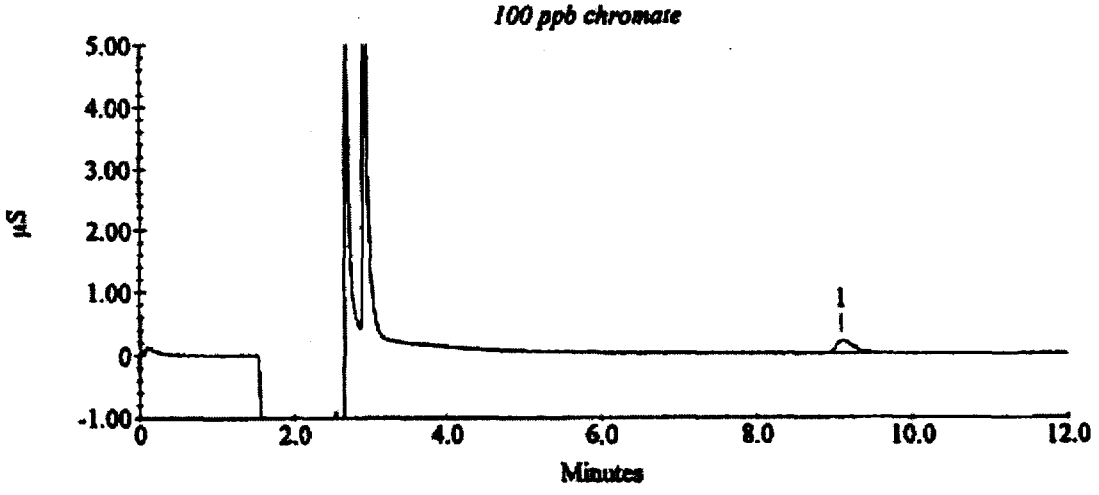
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.12	0.00	34435	2130



100 ppb chromate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

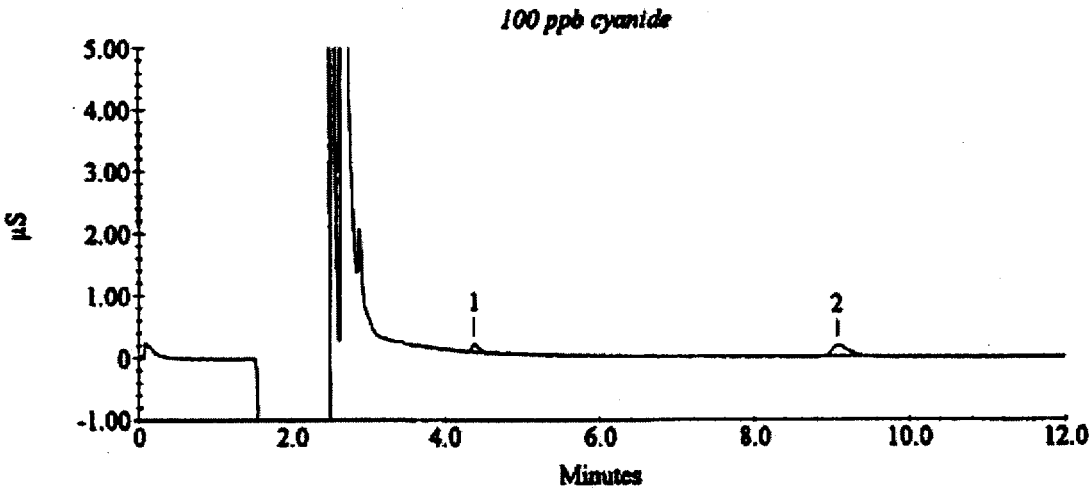
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.08	0.00	32585	1965



100 ppb cyanide in the presence of 20 ppb perchlorate

Peak Information : All Peaks

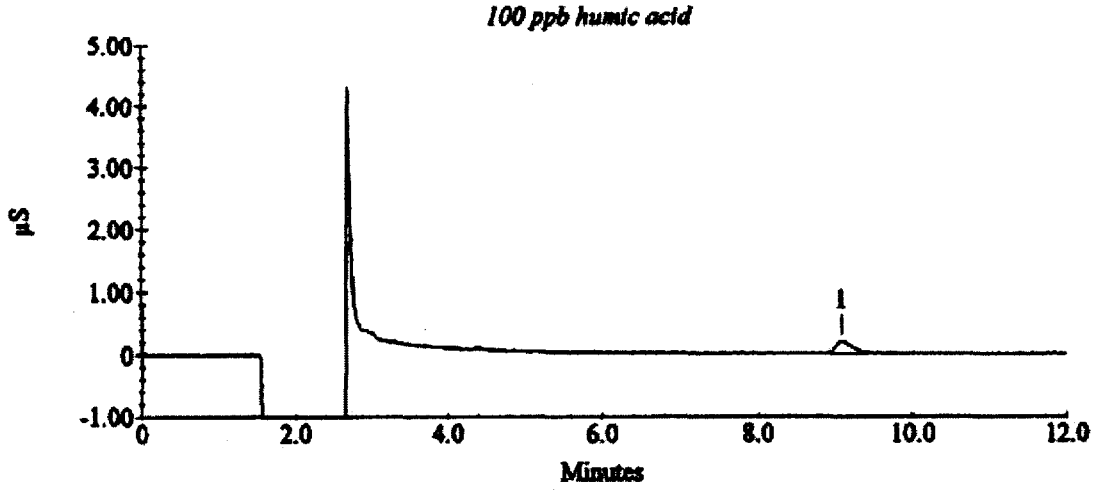
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1		4.38	0.00	7867	1268
2	perchlorate	9.08	0.00	24770	1724



100 ppb humic acid in the presence of 20 ppb perchlorate

Peak Information : All Peaks

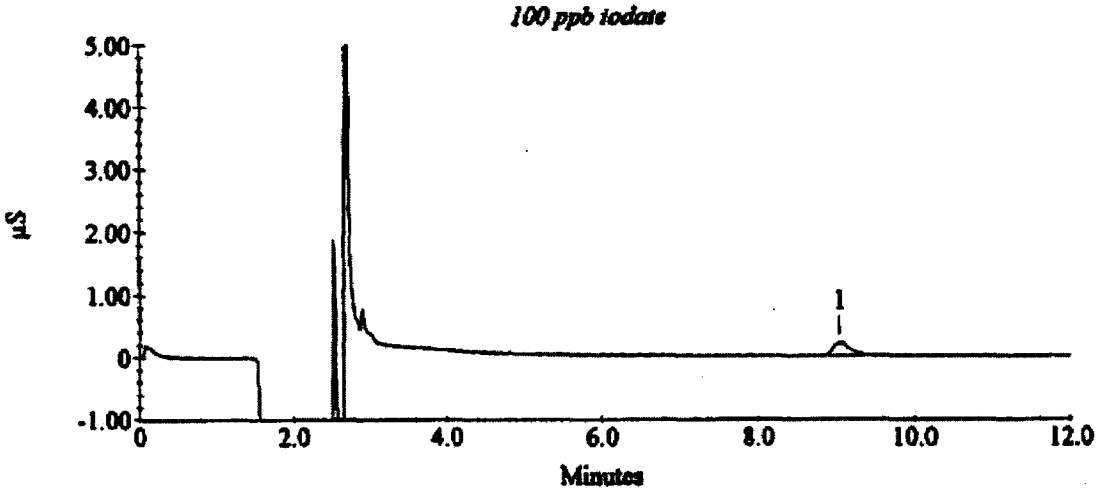
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.08	0.00	30082	1914



100 ppb iodide in the presence of 20 ppb perchlorate

Peak Information : All Peaks

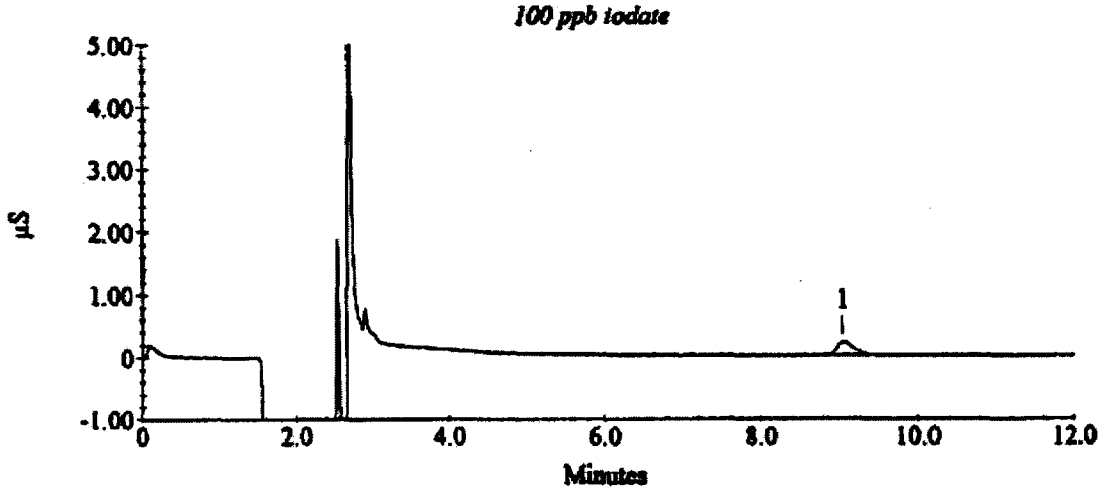
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	34029	2179



100 ppb iodate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

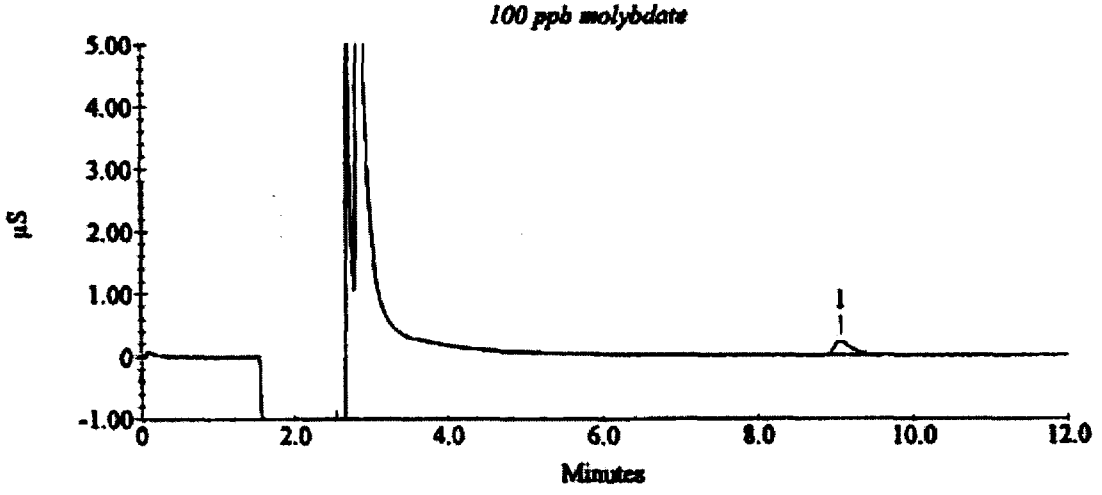
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	34029	2179



100 ppb molybdate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

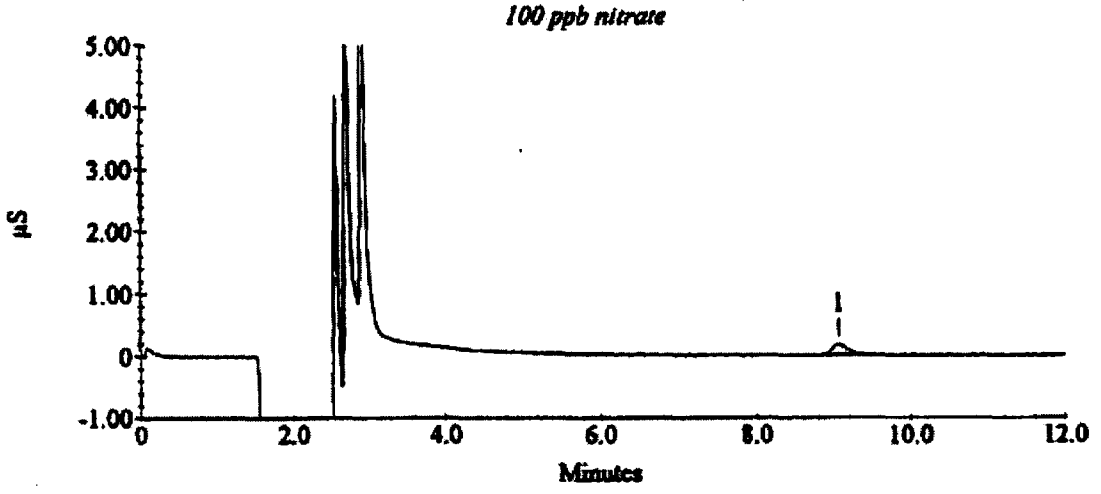
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.07	0.00	32420	2048



100 ppb nitrate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

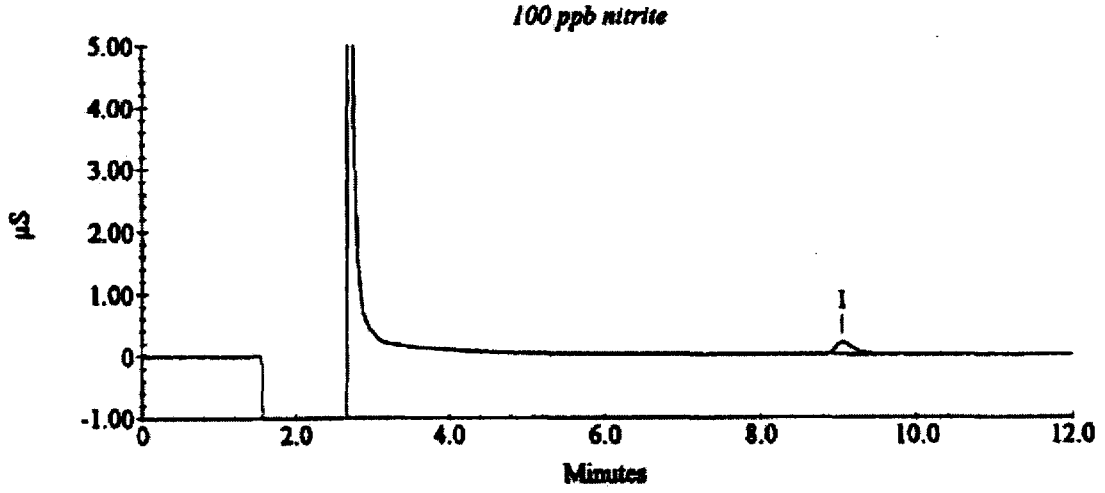
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.07	0.00	24704	1660



100 ppb nitrite in the presence of 20 ppb perchlorate

Peak Information : All Peaks

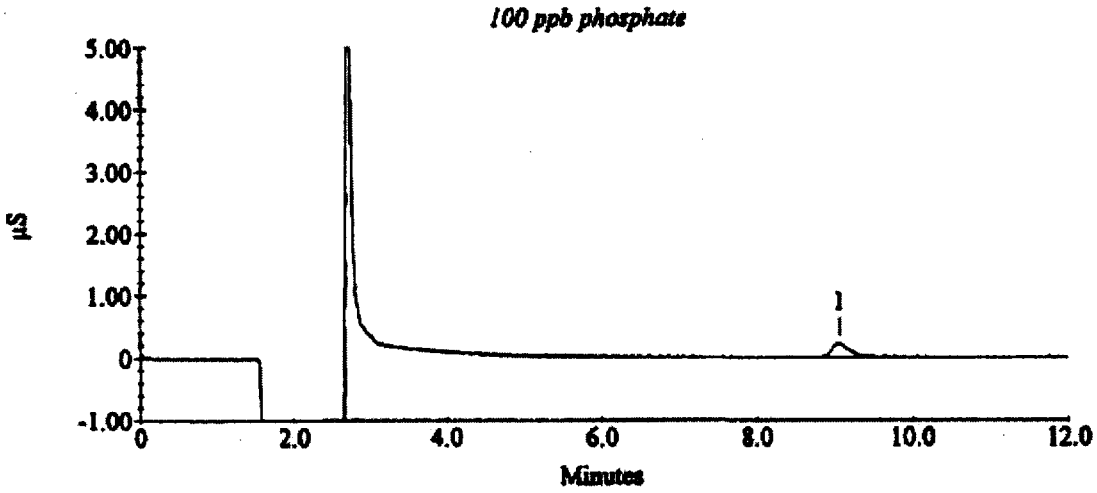
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	30763	2047



100 ppb phosphate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

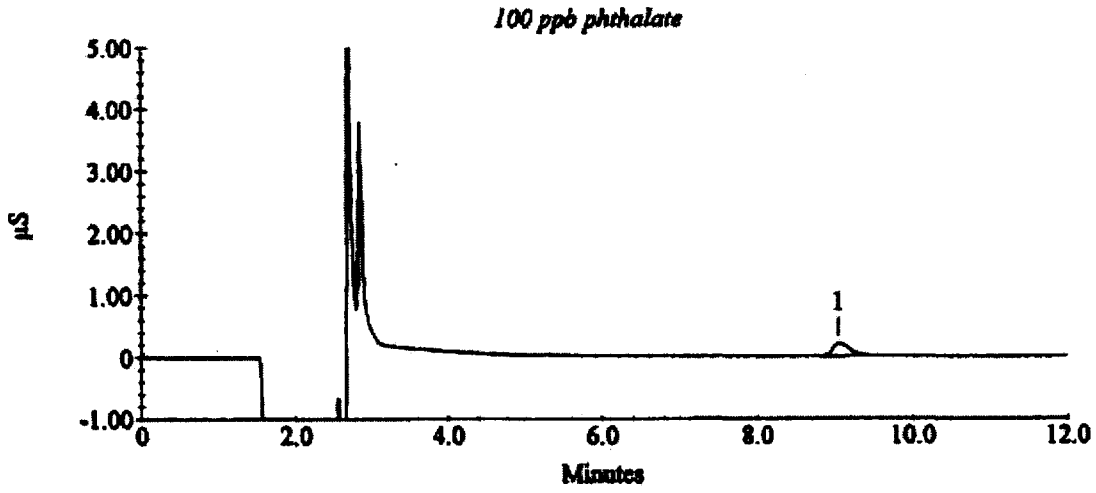
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.07	0.00	33653	2184



100 ppb phthalate in the presence of 20 ppb perchlorate)

Peak Information : All Peaks

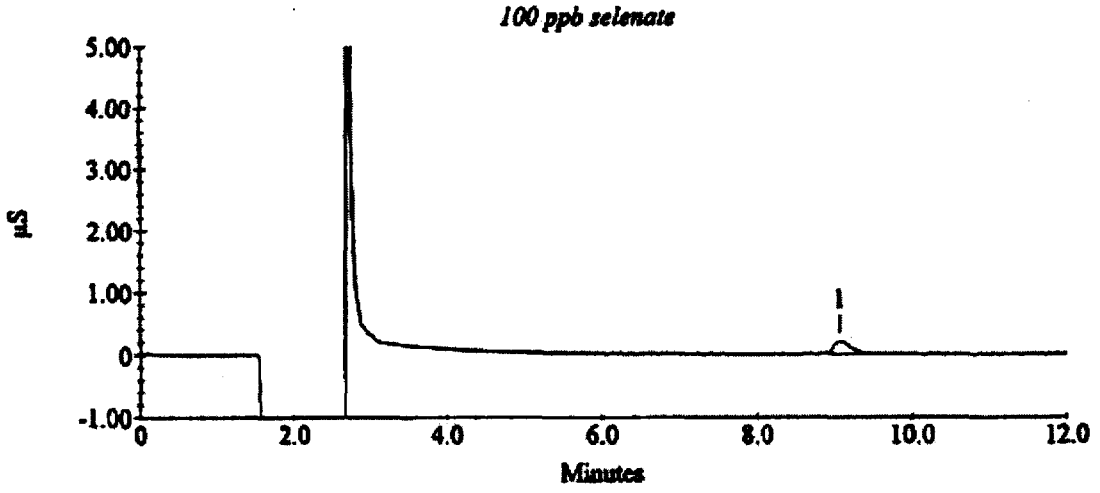
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	32333	2051



100 ppb selenate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

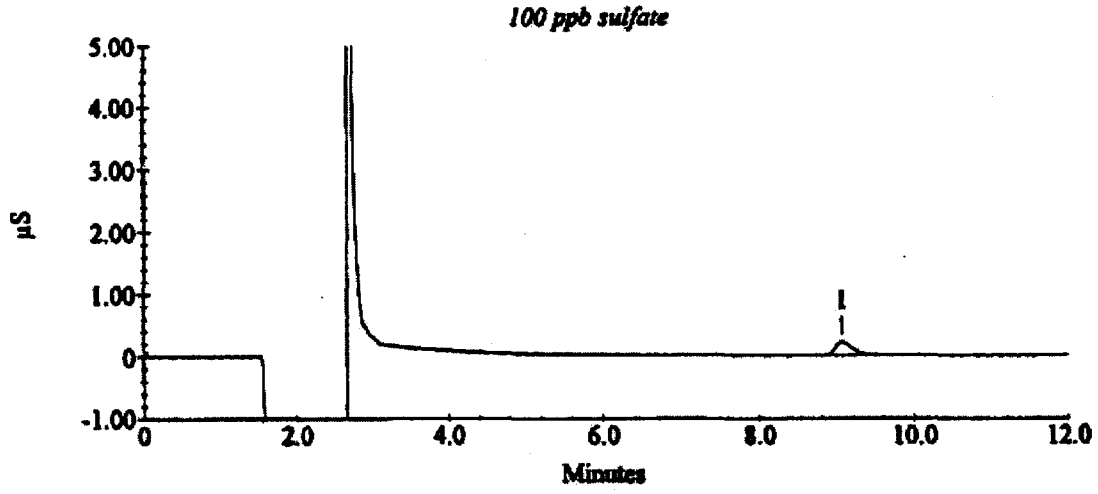
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.07	0.00	31536	2020



100 ppb sulfate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

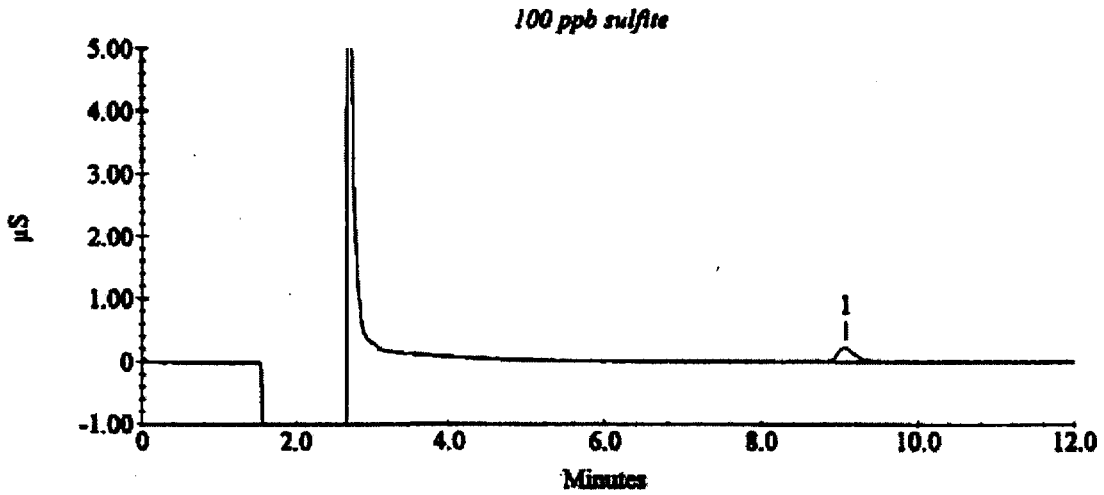
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.07	0.00	35291	2130



100 ppb sulfite in the presence of 20 ppb perchlorate

Peak Information : All Peaks

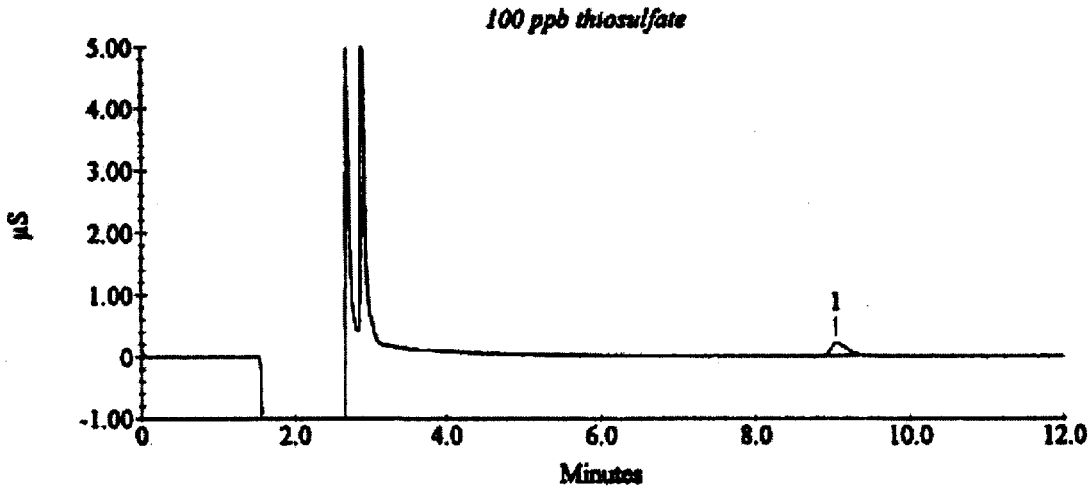
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.08	0.00	34361	2191



100 ppb thiosulfate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

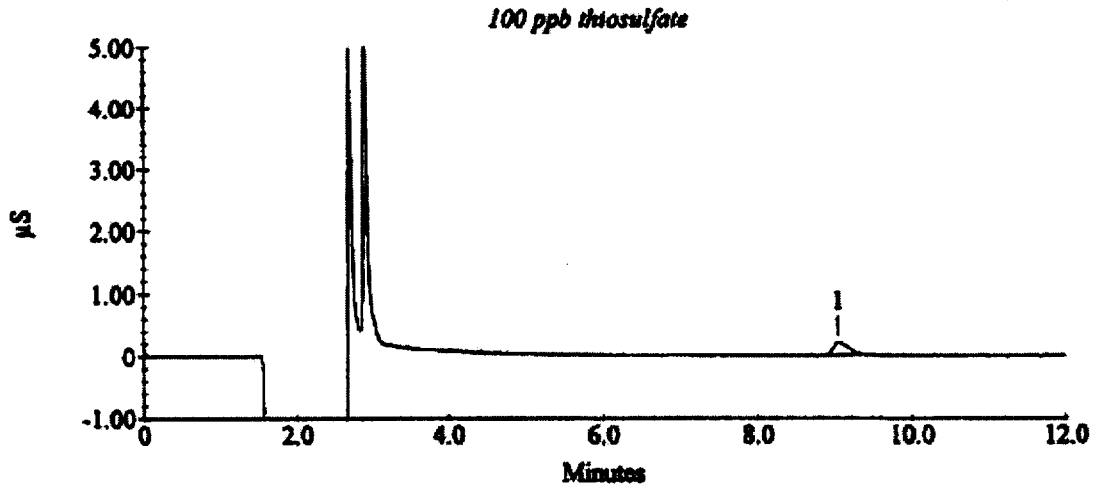
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	29410	2063



100 ppb thiocyanate in the presence of 20 ppb perchlorate

Peak Information : All Peaks

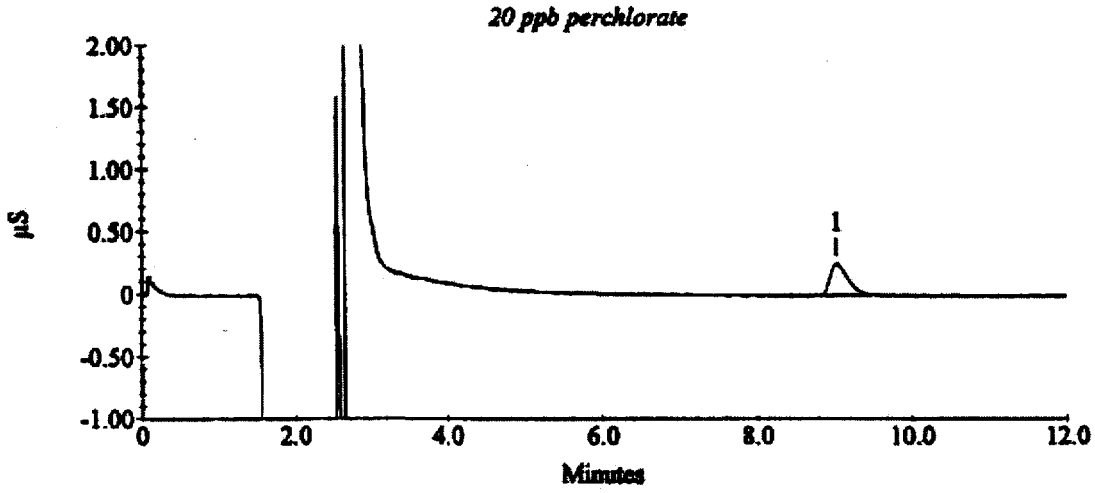
Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	perchlorate	9.05	0.00	29410	2063



20 ppb perchlorate

Peak Information : All Peaks

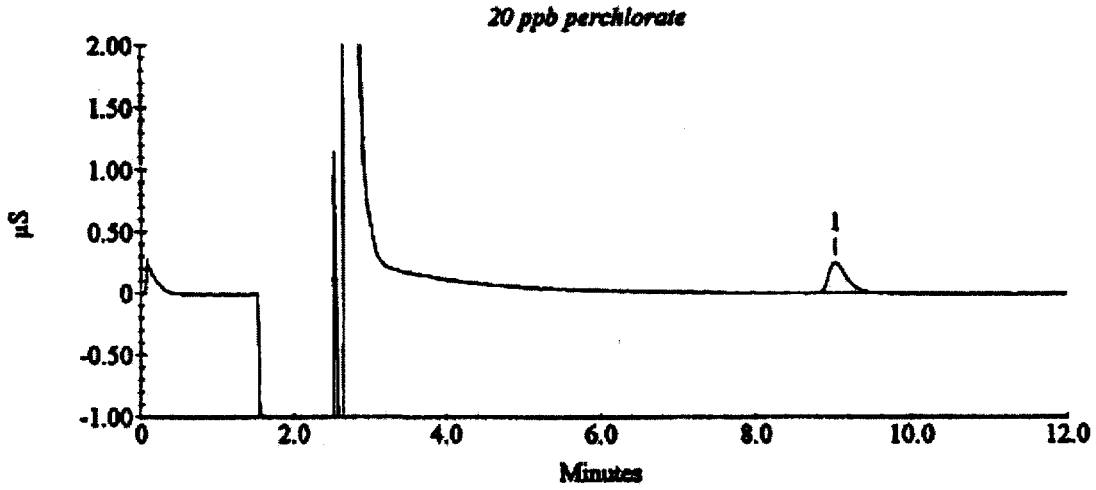
Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.03	19.06	38751	2462



20 ppb perchlorate

Peak Information : All Peaks

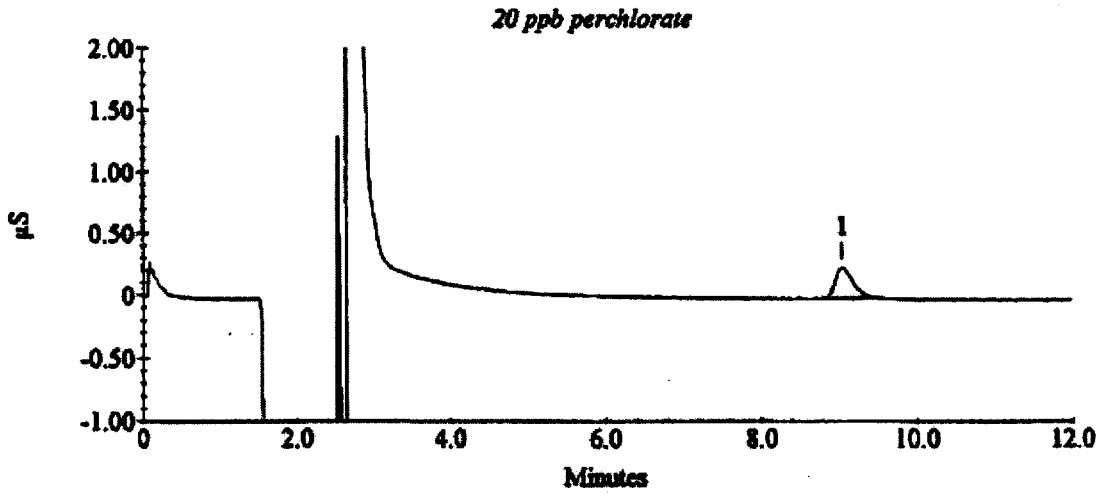
Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.03	19.15	38917	2406



20 ppb perchlorate

Peak Information : All Peaks

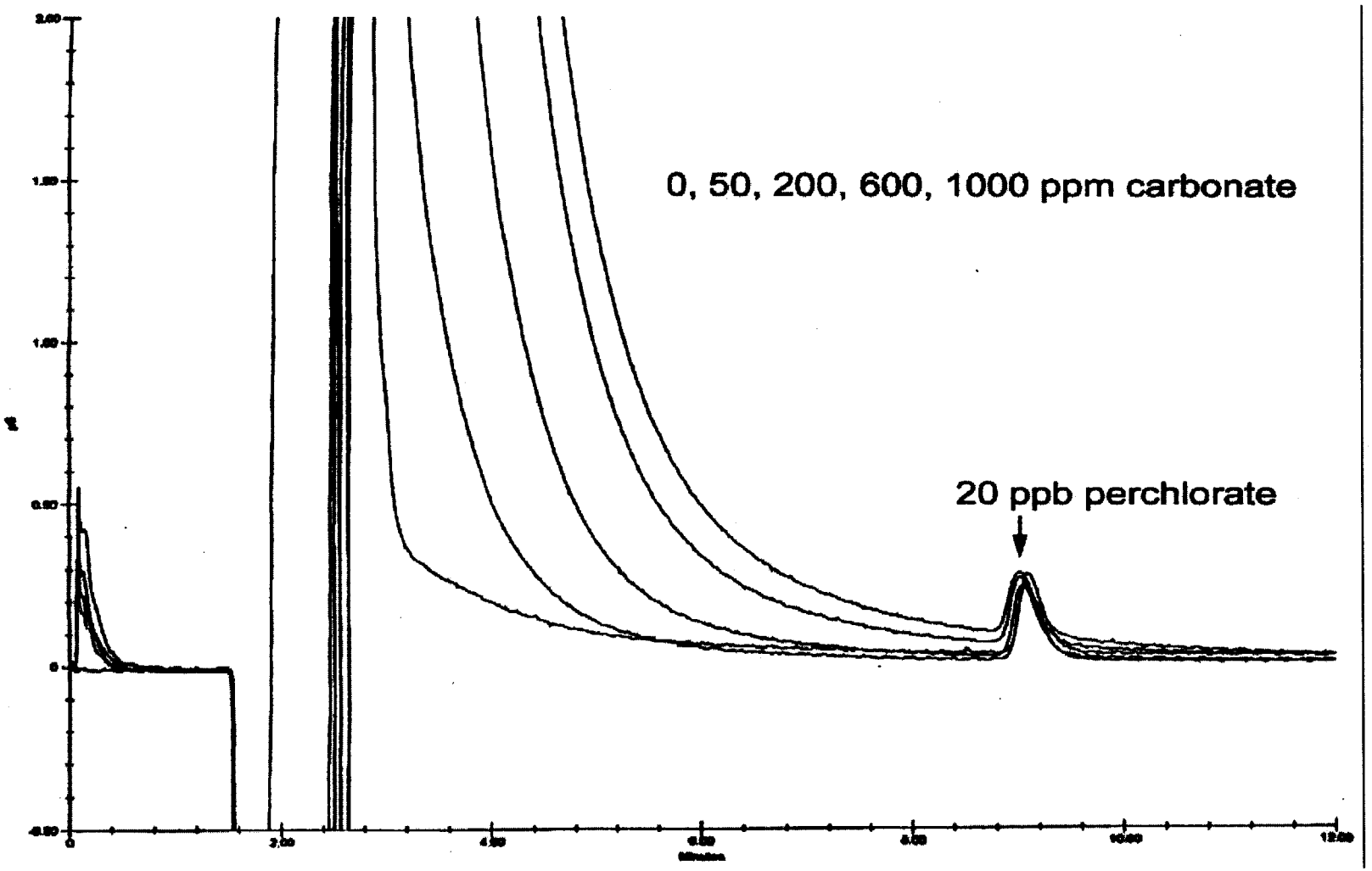
Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.05	18.54	37692	2419



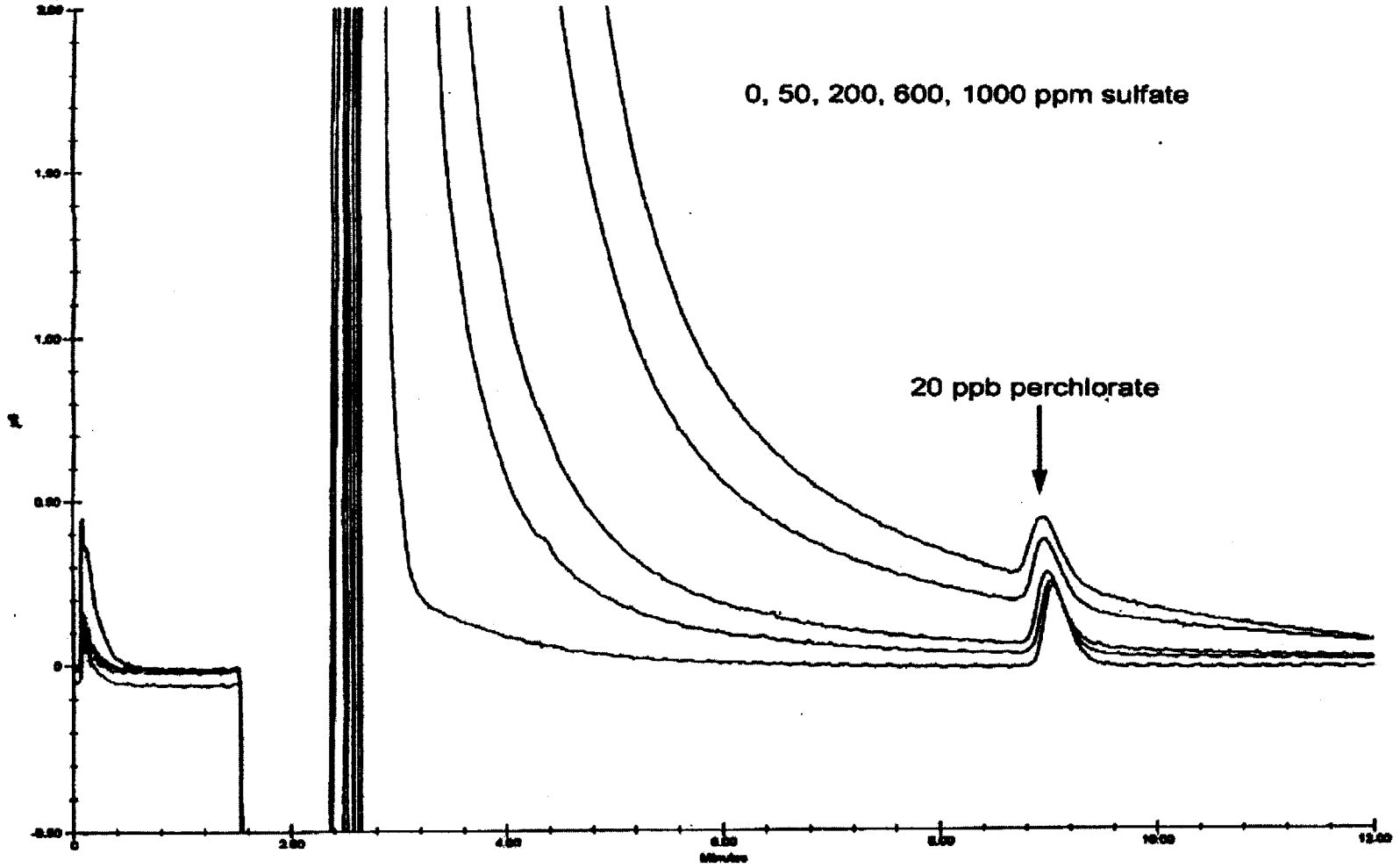
APPENDIX G

STACK PLOTS OF 20 PPB PERCHLORATE SPIKED IN VARIOUS CONCENTRATIONS OF ANIONS

20 ppb perchlorate in the presence of 0, 50, 200, 600, and 1000 ppm carbonate



20 ppb perchlorate in the presence of 0, 50, 200, 600, and 1000 ppm sulfate



20 ppb perchlorate in the presence of 0, 50, 200, 600, and 1000 ppm chloride